TECHNICAL METHODS OF CHEMICAL ANALYSIS

LUNGE AND KEANE'S

TECHNICAL METHODS

OF

CHEMICAL ANALYSIS

SECOND EDITION

EDITED BY

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PREFACE

As in previous volumes of the present edition of *Technical Methods of Chemical Analysis*, all the sections have been thoroughly revised and several completely rewritten so as to include the newer methods of analysis, especially those which have been worked out and accepted in connection with modern developments of chemical industry.

The sections on clays and clay products in the former edition have been rearranged under the heading of Clays, Ceramic Products and Refractories, and the methods of examination subdivided into chemical and physical. The section on Glass has been considerably extended, and in that on Air the most recent methods of determination both of gaseous and of other impurities have been included. In each of the remaining sections special attention has been given to the co-ordination of the subject-matter and to the inclusion of the latest British and American methods of analysis.

Numerical data have been calculated from the atomic weights published by the International Union in 1925, with such approximations as are usual, though empirical factors are retained where they are commonly used in technical work. Temperatures are stated in degrees Centigrade unless other scales are specially indicated.

The Editors desire to record their thanks to the following firms and other organisations for the loan of blocks or drawings or for permission to reproduce illustrations or other matter from their publications:—The American Ceramic Society, Messrs Baird & Tatlock, The British Engineering Standards Association, Messrs Casella, The Ceramic Society, The Chemical Catalog Co., Messrs A. Gallenkamp & Co., Messrs Griffin & Tatlock, H.M. Stationery Office, Messrs Steel and Cowlishow, and Messrs John Wiley & Sons.

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ABBREVIATED TITLES OF JOURNALS

ABBREVIATIONS.	JOURNALS.
Amer. Chem. J.	American Chemical Journal
Amer. J. Sci.	American Journal of Science
Annalen	Annalen der Chemie
Ann. Physik	Annalen der Physik
Ann. Chim. anal.	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie et à la Biologie
Annali Chim. Appl.	Annali di Chimica Applicata
Ann. Chim. Phys.	Annales de Chimie et de Physik
Ann. Falsif.	Annales des Falsifications
Apoth.-Zeit.	Apotheker-Zeitung
Arch. Pharm.	Archiv der Pharmacie
A. S. T. M. Standards	Standards of the American Society for Testing Materials
Atti R. Accad. Lincei	Atti della Reale Accademia dei Lincei
Berg u. Hütten. Zeit.	Berg und Hüttenmännische Zeitung
Ber.	Berichte der deutschen chemischen Gesellschaft
Ber. deut. Keram. Ges.	Berichte der deutschen Keramischen Gesellschaft
Ber. deutsch. Physik. Ges.	Berichte der deutschen physikalischen Gesellschaft
B.E.S.A. Spec.	Specification of the British Engineering Standards Association
B. P.	British Patent
Brit. Assoc. Rep.	Report of the British Association for the Advancement of Science
Bull. Assoc. Belg. des Chim.	Bulletin de l'Association Belgique des Chimistes
Bull. Assoc. Chim. Sucr.	Bulletin de l'Association chimique de Sucre et de Distillerie
Bull. Soc. Chim. Belg.	Bulletin de la Société chimique de Belgique
Bull. Soc. Chim.	Bulletin de la Société chimique de Paris
Bull. Soc. Ind. Nord	Bulletin de la Société Industrielle du Nord de la France
Bur. Stand. J. Res.	Bureau of Standards Journal of Research
Bur. Stand. Sci. Paper	Scientific Paper of the Bureau of Standards
Chem. News	Chemical News
Chem. Trade J.	Chemical Trade Journal
Chem. Zeit.	Chemiker Zeitung
Chem. Zeit. Rep.	Chemiker Zeitung Repertorium
Chem. Ind.	Chemische Industrie
Chem. Zentr.	Chemisches Zentralblatt
Chem. and Met. Eng.	Chemical and Metallurgical Engineering
Chem. Weekblad	Chemisch Weekblad
Comptes rend.	Comptes rendus hebdomadaires des séances de l'Académie des sciences
Dingl. polyt. J.	Dingler's polytechnisches Journal
Electrochem. Ind.	Electrochemical and Metallurgical Industry
Electrotech. Zeitsch.	Electrotechnische Zeitschrift
Eng. and Min. J.	Engineering and Mining Journal
Fischer's Jahresber.	Fischer's Jahresbericht
Gas J.	Gas Journal

ABBREVIATIONS.	JOURNALS.
Gazz. Chim. Ital.	Gazzetta Chimica Italiana
Ger. Pat.	German Patent
Giorn. Chim. Ind. Appl.	Giornate di Chimica Industriale ed Applicata
Glastechn. Ber.	Glastechniches Berichte
Helv. Chim. Acta	Helvetica Chimica Acta
Ind. Bl.	Industrie Blatt
Ind. Eng. Chem.	Industrial and Engineering Chemistry
Jahresber. d. chem. Techn.	Jahresbericht der chemischen Technologie
Jahresber. d. Pharm.	Jahresbericht der Pharmazie
Jahresber. f. Chem.	Jahresbericht für Chemie
J. Agric. Sci.	Journal of Agricultural Science
J. Amer. Ceram. Soc.	Journal of the American Ceramic Society
J. Amer. Chem. Soc.	Journal of the American Chemical Society
J. Anal. and Applied Chem.	Journal of Analytical and Applied Chemistry
J. Assoc. Off. Agric. Chem.	Journal of the Association of Official Agricultural Chemists
J. Chem. Met. Soc., S. Africa	Journal of the Chemical, Metallurgical, and Mining Society of South Africa
J. Chem. Soc.	Journal of the Chemical Society
J. Chem. Soc. Abstr.	Journal of the Chemical Society, Abstracts
J. Franklin Inst.	Journal of the Franklin Institute
J. Gasbeleucht.	Journal für Gasbeleuchtung und Wasserversorgung
J. Gas Lighting	Journal of Gas Lighting
J. Inst. Brewing	Journal of the Institute of Brewing
J. Inst. Chem.	Journal and Proceedings of the Institute of Chemistry
J. Inst. Mech. Eng.	Journal of the Institution of Mechanical Engineers
J. Inst. Metals	Journal of the Institute of Metals
J. Iron and Steel Inst.	Journal of the Iron and Steel Institute
J. Oil and Col. Chem. Assoc.	Journal of the Oil and Colour Chemists Association
J. Pharm. Chim.	Journal de Pharmacie et de Chimie
J. Phys. Chem.	Journal of Physical Chemistry
J. Physik	Journal der Physik
J. Physique	Journal de Physique et le Radium
J. prakt. Chem.	Journal für praktische Chemie
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia
J. Soc. Arts	Journal of the Royal Society of Arts
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry
J. Soc. Chem. Ind. Japan	Journal of the Society of Chemical Industry of Japan
J. Soc. Glass Tech.	Journal of the Society of Glass Technology
Kolloid Z.	Kolloid Zeitschrift
Landw. Versuchs-Stat.	Die landwirthschaftlichen Versuchs-Stationen
Mitt. k. Materialprüf.	Mittheilungen aus dem königlichen Materialprüfungsamt zu Gross-Lichterfelde West
Monatsh.	Monatshefte für Chemie der kaiserlichen Akademie der Wissenschaften, Vienna
Monit. Scient.	Moniteur Scientifique
Nuovo Cimento	Il Nuovo Cimento
Oesterr. Chem. Zeit.	Oesterreichische Chemiker Zeitung
Pharm. J.	Pharmaceutical Journal
Pharm. Rev.	Pharmaceutical Review
Pharm. Weekblad	Pharmazeutisch Weekblad
Pharm. Zeit.	Pharmazeutische Zeitung
Pharm. Zentralh.	Pharmazeutische Zentralhalle
Pharm. Zentr.	Pharmazeutisches Zentralblatt
Phil. Mag.	Philosophical Magazine and Journal of Science
Phil. Trans.	Philosophical Transactions of the Royal Society

ABBREVIATIONS.	JOURNALS.
Phys. Rev.	Physical Review
Proc. Amer. Acad. . . .	Proceedings of the American Academy
Proc. Amer. Electrochem. Soc. .	Proceedings of the American Electrothemical Society
Proc. Amer. Inst. Min. Eng.; Bull. Amer. Inst. Min. Eng. .	Proceedings and Bulletin of the American Institute of Mining Engineers
Proc. Amer. Phil. Soc. . .	Proceedings of the American Philosophical Society
Proc. Amer. Soc. Test. Mats. .	Proceedings of the American Society for Testing Materials
Proc. Inst. Civ. Eng. . . .	Proceedings of the Institution of Civil Engineers
Proc. Inst. Mech. Eng. . .	Proceedings of the Institution of Mechanical Engineers
Proc. Inst. Min. and Met. . .	Proceedings of the Institution of Mining and Metallurgy
Proc. K. Akad. Wetensch. Amsterdam	Koninklijke Akademie van Wetenschappen te Amsterdam, Proceedings (English Edition)
Proc. Phys. Soc.	Proceedings of the Physical Society of London
Rec. trav. chim.	Receuil des travaux chimiques des Pays-Bas et de la Belgique
Rev. intern. Falsif. . . .	Revue internationale des Falsifications
Roy. Soc. Proc.	Proceedings of the Royal Society
Staz. speriment. agr. Ital. . .	Le Stazione sperimentali agrarie Italiane
Tonindustrie Zeit. . . .	Tonindustrie Zeitung
Trans. Amer. Ceram. Soc. . .	Transactions of the American Ceramic Society
Trans. Amer. Electrochem. Soc. .	Transactions of the American Electrochemical Society
Trans. Ceram. Soc. . . .	Transactions of the Ceramic Society
Trans. Faraday Soc. . . .	Transactions of the Faraday Society
Trans. Inst. Min. and Met. . .	Transactions of the Institution of Mining and Metallurgy
U.S. Cons. Reps. . . .	United States Consular Reports
Z. anal. Chem.	Zeitschrift der analytischen Chemie
Z. angew. Chem. . . .	Zeitschrift für angewandte Chemie
Z. anorg. Chem.	Zeitschrift der anorganische Chemie
Z. Elektrochem.	Zeitschrift für Elektrochemie
Zeitschr. f. landw. Versuchswesen, Österr.	Zeitschrift für das landwirtschaftliche Versuchswesen in Österreich
Z. für chem. Apparatenkunde .	Zeitschrift für chemische Apparatenkunde
Z. Instrumentenk. . . .	Zeitschrift für Instrumentenkunde
Z. öffentl. Chem. . . .	Zeitschrift für öffentliche Chemie
Z. physik. Chem. . . .	Zeitschrift für physikalische Chemie
Z. Unters. Nahr. u. Genussm. .	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel
Z. Ver. deut. Zuckerind. . .	Zeitschrift des Vereins der deutschen Zucker-Industrie
Z. Verein. deutsch. Ingen. . .	Zeitschrift des Vereins deutscher Ingenieure
Z. Zuckerind. Böhm. . . .	Zeitschrift für Zuckerindustrie in Böhmen

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Calcareous Cements

Drinking Water and Water Supplies

CLAYS, CERAMIC PRODUCTS AND REFRACTORIES—CHEMICAL EXAMINATION

By H. V. THOMPSON, M.A., Head of the Chemistry Department, North Staffordshire Technical College, Stoke-on-Trent

"THE term *clay* is applied industrially to a fine-grained mixture of various minerals which have these qualities: (1) it is plastic enough to be moulded when it is wet; (2) it retains its shape when dried in spite of a certain amount of contraction; and (3) when the moulded mass is heated at a high enough temperature it sinters together, forming a hard, coherent mass without losing its original contour."[1] It is to these three properties that clays owe their great industrial importance. Clays are formed by the action of weathering agents upon felspathic rocks such as granites, which may decompose under suitable conditions into clay admixed with varying amounts of the more resistant varieties of mica, quartz and other minerals from the disintegrated rock mass. Some clays are found *in situ*, while others have been transported by running water and redeposited at lower levels, but, whatever its subsequent history may be, it is obvious from the mode of formation that no clay is chemically homogeneous. Transported clays have usually, though not necessarily, more mineral impurities than residual clays.

The purest kinds of china clay approximate closely in composition to Al_2O_3, $2SiO_2$, $2H_2O$ and it has been assumed that the common constituent of all clays and the one to which their plasticity is primarily due is a colloidal alumino-silicate of this composition for which the term clayite has been adopted to distinguish it from the crystalline mineral, kaolinite, of the same composition.

The minerals normally associated with a clay may produce a physical effect by decreasing its plasticity owing to their crystalline nature and also act chemically as fluxes when the clay is fired. The usual fluxing oxides found in a clay are those of the alkalis and alkaline earths and iron, while at high temperatures silica also acts as a flux. The presence of an excess of silica likewise intensifies the effect of the other fluxes. The most refractory clays are consequently those which approximate most closely in composition to clayite, *viz.*, Al_2O_3, 39·48; SiO_2, 46·56; H_2O, 13·96 per cent.

[1] J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, 1925, 6, 471.

It must be borne in mind that the chemical analysis of a clay is not an infallible criterion of its suitability for ceramic purposes since instances are known in which two clays of almost identical composition have to be classed as worthless and high grade respectively when physical tests are applied.

In addition to typical clays, other materials commonly used in the manufacture of ceramic products and refractories are: (1) felspars; (2) bauxites, calcined alumina and alundum; (3) limestones, dolomites and magnesites; (4) barytes; (5) zirconium minerals; (6) chromite; (7) fluorspar and cryolite. The general methods of analysis for clays are to a certain extent applicable to some of these materials; the modifications of the typical clay analysis and the special methods required in individual cases are given below.

Among the finished products which are usually subjected to chemical analysis, the following are the most important: (1) silica, magnesite, chromite, zirconia and fire bricks; (2) earthenware, china and insulator bodies; (3) glazes; (4) colours.

I. FIRECLAYS, RAW GANISTERS, QUARTZOSE ROCKS AND MANUFACTURED PRODUCTS

Sampling. In every case, whatever may be the substance under investigation, it is imperative to sample carefully the finely-ground material, otherwise the analysis will not be a representative one, and consequently of little value. (See Vol. I., pp. 4-10.)

Determination of Hygroscopic Moisture. About 5 g. of the finely-ground material is dried in an air bath or toluene oven at 105° to 110°, until there is no further loss in weight (about three to four hours is generally sufficient). It is not usual to determine the hygroscopic moisture, as normally the analysis is made on the dried sample.

Determination of Loss on Ignition. One g. of the dry material is heated in a platinum crucible for fifteen minutes over a small flame, then for thirty minutes over a good Méker burner, with the lid on for the last ten minutes. The crucible and contents are cooled in a desiccator, weighed, again heated for ten minutes over the Méker burner and the weight again checked after cooling.

Low results are usually due to the incomplete combustion of carbonaceous matter, whereas losses by spurting, produced by too rapid ignition (especially if carbonates are present), generally account for high results.

1. Determination of Silica

The ignited material[1] in the platinum crucible is intimately mixed with 10 to 15 g. of anhydrous sodium carbonate. The lid is placed

[1] Some analysts prefer to weigh out a fresh gram of the dry, unignited material.

on the crucible and the mixture *gently* heated over a Méker burner and finally fused at a bright red heat until the contents are in a state of quiet fusion—about fifteen to thirty minutes is required. The crucible is allowed to cool on a clean, *unglazed* tile; it is then half-filled with water and carefully heated over the tip of a small flame whereby the cake can usually be detached *en bloc* from the crucible. The cake and washings from the crucible are placed in a *dry* 350 c.c. basin glazed on the inside only; after adding about 150 c.c. of water the basin is covered with a clock glass and 30 to 35 c.c. of concentrated hydrochloric acid is added from a pipette through the lip of the basin. When the first violent reaction is over the basin is warmed on a water-bath until all action has ceased and the cake has disintegrated. Any drops on the under side of the clock glass are rinsed into the basin; the platinum crucible and lid are washed with dilute hydrochloric acid and hot water and the washings also poured into the basin. The cake is now crushed to powder with a small agate pestle and the solution evaporated to dryness on a water-bath until the smell of hydrochloric acid is no longer perceptible. When crystallisation has started, the semi-solid mass must be repeatedly broken up with the end of a glass rod. The basin and contents are covered with a clock glass and then baked in an air oven at 110° for one hour. The baked mass is moistened with concentrated hydrochloric acid, about 75 c.c. of hot water added, the liquid filtered and the residue washed with hot water until free from chlorides. The filtrate is returned to the basin, again evaporated to dryness, baked, digested with hydrochloric acid and hot water and filtered as in the first instance. The wet filter papers are transferred to a weighed platinum crucible and carefully dried and charred *without ignition* over a burner with a mushroom head. The carbon is burnt off slowly and the crucible and contents finally ignited to constant weight over the full heat of a Méker burner, with the lid in position for the last ten minutes.

The crucible is weighed and the result entered as "weight of crucible plus silica and residue." The silica contains traces of the oxides of aluminium, iron and titanium; accordingly it is treated with about 5 c.c. of water and a few drops of concentrated sulphuric acid (to prevent the volatilisation of titanic fluoride at red heat). About 15 c.c. of hydrofluoric acid is added, a few drops at a time, and, after placing the crucible *eccentrically* on a sand-bath, the solution is slowly evaporated to dryness. The outside of the crucible is then freed from sand, the crucible ignited for five minutes and weighed when cool. The result is recorded as "weight of crucible plus residue." The difference between the two weighings gives the amount of silica in the sample. Subsequently the ammonia precipitate is ignited in this crucible *with the silica residue.*

Normally the weight of the silica residue does not exceed 10 mg.: a residue much in excess of this figure usually indicates the presence of barium sulphate or of relatively large quantities of titanic or zirconium oxides in the material under analysis. In such cases the silica residue is fused with a small quantity of sodium bisulphate, the cake extracted and digested with a little dilute sulphuric acid until completely disintegrated. The solution is filtered; the residue washed free from sulphates, ignited and weighed as barium sulphate. The filtrate is added to the main bulk of filtrate from the silica.

2. The Ammonia Precipitate

The filtrate from the silica is heated to 80° to 90° and 2 to 3 g. of solid ammonium chloride added to it, followed by a slight excess of concentrated ammonia, drop by drop; the solution is simultaneously stirred well and then filtered, after standing for five minutes. If the clay contains manganese (which will be indicated by the green colour of the cake after fusion with sodium carbonate), 2 to 3 c.c. of bromine water is added to the solution before the two ammonia precipitations, otherwise the procedure is as described above. The precipitate is *immediately* washed four or five times with hot water; a hole is made in the apex of the filter paper and the precipitate washed back into the beaker from which it has just been filtered. The filter paper is then washed free from chlorides and *kept for ignition*. The precipitate is redissolved in a slight excess of concentrated hydrochloric acid, the solution heated to 80° to 90° and again precipitated by adding excess of ammonia, drop by drop, with constant stirring. The liquid is filtered into the beaker containing the first filtrate and the precipitate washed repeatedly with *small* quantities of a hot alkaline solution of ammonium nitrate (2 to 3 g. per litre made just alkaline with ammonia) until free from chlorides, but *on no account must the ammonia precipitate be allowed to run dry.*

When the ammonia precipitate does not exceed 5 per cent. only a slight excess of ammonia is added to the filtrate from the silica and the excess is boiled off. One precipitation only is necessary.

The filtrate is evaporated to about 100 c.c. and 2 to 3 c.c. of ammonia added. The liquid is filtered and the small precipitate washed free from chlorides with the ammonium nitrate solution. The filtrate is kept for the determination of lime and magnesia. The three filter papers used in the ammonia precipitation are transferred to the crucible containing the silica residue and the papers are slowly dried and charred over a mushroom-headed burner. The temperature is then raised until all the carbon is burnt off and the crucible finally heated with the lid on over a Méker burner until its weight is constant.

After weighing, the ignited oxides are *very slowly* dissolved in the crucible by fusion with 6 to 8 g. of pure fused potassium bisulphate.

The cake when cold is detached from the crucible and transferred to a porcelain basin and about 150 c.c. of water and 20 c.c. of concentrated sulphuric acid added to it; the crucible is well rinsed out with hot water and the washings poured into the basin. The mixture is heated on a water-bath until all is dissolved; the solution is then diluted to 250 c.c. in a graduated flask to give the stock solution for the estimation of iron and titanium oxides.

Colorimetric Estimation of Ferric Oxide. When the amount of ferric oxide does not exceed about 5 per cent. a colorimetric process is used, while larger amounts are estimated volumetrically (see p. 6). The colour of the sample in the crucible after the determination of the loss on ignition is a good criterion as to which process is the better. For the colorimetric determination an aliquot portion of the stock solution, obtained from the bisulphate fusion, is diluted to 250 c.c. to give the test solution. Twenty-five c.c. is taken for a normal clay, or other material, containing 1 per cent. or less of ferric oxide.

The following stock solutions are required:—

Standard Iron Solution. 0·6040 g. of *pure* ammonium ferric alum is dissolved in water, 5 c.c. of concentrated sulphuric acid added, and the solution diluted to a litre in a graduated flask. 1 c.c. = 0·0001 g. Fe_2O_3.

Potassium Thiocyanate Solution. 97 g. (1 g. mol.) of the salt per litre.

Potash Alum Solution. 0·05 g. of alumina, prepared by strongly igniting *pure* ammonium alum in a platinum dish, is fused with 5 g. of potassium bisulphate: the cold cake is extracted with water, 10 c.c. of concentrated sulphuric acid is added, and the solution is made up to 1 litre. The solution is used to counteract the effect of the aluminium sulphate in the test solution on the tint of the ferric thiocyanate.

Five c.c. of the standard iron solution is diluted to 100 c.c. and transferred to a burette reading to 0·1 c.c., while a similar burette is filled with distilled water. Two small specimen glasses, preferably with parallel sides (*e.g.*, the test glasses of a colorimeter), are respectively filled with a mixture of (*a*) 10 c.c. of the potassium thiocyanate solution with 10 c.c. of the buffer solution of potash alum and (*b*) 10 c.c. of potassium thiocyanate solution with 10 c.c. of the test solution. The diluted standard iron solution is added from the burette to the potash alum solution and an equivalent amount of distilled water from the other burette to mixture (*b*)—stirring thoroughly after each addition—until the tints in the two test glasses are the same. The tints are viewed against a neutral background by light transmitted through the sides of the glasses. If more than 6 to 8 c.c. of the diluted iron solution is taken, errors are likely to result owing to the difficulty in judging the equality of tint in concentrated solutions of ferric thiocyanate. A weaker test solution must then be made by diluting 10 or 5 c.c. of the stock solution to 250 c.c.

Calculation. Using 1 g. of material and the above-mentioned dilutions, the percentage of Fe_2O_3 is given by $V/8$, where V is the

number of c.c. of diluted standard iron solution required to give a match in colour: if w g. of material is taken and if the 250 c.c. of test solution contains v c.c. of the stock solution, the percentage of Fe_2O_3 is $25\,V/8vw$.

Volumetric Estimation of Ferric Oxide. One hundred c.c. of the stock solution obtained from the fusion of the mixed oxides with potassium bisulphate is reduced with about 10 g. of zinc (iron-free) or 4 g. of magnesium stick in a flask fitted with a Bunsen valve and the reduced solution titrated with a standard solution of potassium permanganate. The strength of the permanganate solution used depends upon the amount of ferric oxide present: for 5 to 10 per cent. of ferric oxide $N/50$ permanganate is a convenient strength.

The presence of titanic oxide introduces a disturbing effect as more or less of it is simultaneously reduced to titanium sesquioxide which is re-oxidised on titration, thus increasing the apparent amount of ferric oxide. The reduced solution is, therefore, treated with a small quantity of bismuth oxide whereby the sesquioxide is alone re-oxidised. The solution after treatment is rapidly passed under suction through a Jena glass filter funnel into a filter flask. The flask from which the solution is filtered as well as the filter funnel are thoroughly washed with dilute sulphuric acid. To prevent atmospheric oxidation of the ferrous iron the filtration is carried out in an atmosphere of carbon dioxide. This is maintained by placing a few chips of iron-free magnesite in the reduced solution, the filter funnel and the filter flask, a little dilute sulphuric acid being added to the magnesite in the latter a few minutes before filtration.

The amount of metal taken for the reduction should be noted and a blank titration made on an equal quantity of metal dissolved in dilute sulphuric acid, the solution being filtered before titration if any carbon separates out. The difference between the two titrations gives the volume of permanganate actually consumed in the oxidation of the ferrous iron. A duplicate estimation can be made by again reducing the oxidised solution and repeating the whole process.

An alternative method is to estimate the ferric iron directly by reduction with a standard solution of titanous chloride. Full details for the titration are given in *New Reduction Methods in Volumetric Analysis*, by E. Knecht and E. Hibbert. The advantages of this process are—(*a*) no preliminary reduction of the iron to the ferrous state is necessary; (*b*) titanic salts are not simultaneously reduced with the ferric iron. On the other hand, the titanous chloride solution must be re-standardised before each estimation.

Estimation of Titanic Oxide. Fifty c.c. of the stock solution, obtained from the bisulphate fusion, is pipetted into a 100 c.c. graduated flask, 10 c.c. of 20 vol. hydrogen peroxide (free from

fluorides) added, followed by 5 c.c. of conc. sulphuric acid, and the mixture made up to the mark. Five c.c. of standard titanium solution and 10 c.c. of hydrogen peroxide are similarly diluted to 100 c.c. A test glass is *about* half filled with the solution to be tested. Ten c.c. of diluted standard titanium solution is pipetted into another glass and water added to it from a burette until the tints of the two liquids, compared as indicated in the previous estimation, match.

Standard Titanium Solution. One g. of *pure* titanic oxide is fused with 10 g. of potassium bisulphate. The cold cake is extracted with water and 20 c.c. of concentrated sulphuric acid added. The mixture is gently warmed on a water-bath until the cake has completely dissolved when the solution is diluted to a litre. One c.c. = 0·001 g. TiO_2.

Calculation. If 1 g. of material is taken, with the dilutions given above, the percentage of TiO_2 is $25/(10+V)$ where V is the number of c.c. of water added to the 10 c.c. of diluted standard titanium solution to produce equality of tint. When w g. of material is taken and v c.c. of the stock solution is diluted to 100 c.c. the percentage is $1250/(10+V)\,vw$.

The weight of the ammonia precipitate less the weights of the ferric and titanic oxides and the *filter ashes, including those used in the silica estimation*, gives the weight of alumina in the sample.

Colorimetric Estimation of Manganous Oxide. The percentage of manganous oxide, though rarely required in a clay analysis, can be estimated in the following way:—

Preparation of the standard permanganate solution. A solution containing 0·1 g. of manganous oxide per litre is prepared by dissolving 0·3145 g. of *pure* manganous sulphate ($MnSO_4,4H_2O$) in water, acidifying the solution with a few c.c. of concentrated sulphuric acid and diluting to 1 litre. A suitable quantity—say 5 c.c. —of the above solution is pipetted into a 100 c.c. flask and to it is added 10 c.c. of a 0·2 per cent. solution of silver nitrate, followed by 1 g. of ammonium persulphate. The flask is heated on a water-bath until a pink colour is developed; by the time the contents of the flask have cooled the colour will have reached its maximum intensity, when the solution is diluted to 100 c.c. A brown precipitate on oxidation with ammonium persulphate shows that insufficient silver nitrate has been used, in which case the solution is reduced by adding a few c.c. of sulphurous acid and again re-oxidised after the addition of another 10 c.c. of the silver nitrate solution.

Preparation of the test solution. The stock solution resulting from the fusion of the mixed oxides with potassium bisulphate is used for the test. As this solution generally contains chlorides, which interfere with the test, 100 c.c. of it is boiled and the chlorides precipitated by the addition of silver nitrate. The solution is filtered and the

precipitate washed, both filtrate and washings being collected in a 200 c.c. flask. The filtrate is acidified with sulphuric acid, 10 c.c. of 0·2 per cent. silver nitrate solution and 1 g. of ammonium persulphate are then added and the mixture warmed as in the preparation of the standard permanganate solution. When cool the solution is diluted to the 200 c.c. mark.

One of the test glasses of a colorimeter is *about* half filled with this solution and into the other test glass 10 c.c. of the standard permanganate solution is pipetted. Water is next added from a burette to the standard solution until equality in tint results. If the volume of water taken is v c.c., then with the dilutions given above the percentage of manganous oxide reduces to $2{\cdot}5/(10+v)$.

3. Determination of Lime

The filtrate from the ammonia precipitate is boiled for a few minutes with 1 to 3 g. of ammonium oxalate and 5 to 10 c.c. of concentrated ammonia added; after stirring well, the mixture is warmed on a water-bath for two hours. The liquid is filtered, the precipitate washed two or three times and the filtrate reserved for the magnesia estimation. A hole is made in the filter paper, the precipitate washed into the beaker from which it has been filtered and redissolved in a few c.c. of nitric acid, the filter paper being rejected. The solution is boiled, again precipitated and warmed for two hours as before, after which it is filtered and the precipitate washed free from chlorides. The precipitate is slowly dried and ignited in a platinum crucible and then heated over a Méker burner for fifteen minutes, with the lid on the crucible for the last five minutes. The crucible, when cool, is *rapidly* weighed, again ignited for five minutes and the weight checked.

4. Estimation of Magnesia

The *first* filtrate from the ammonium oxalate precipitate is boiled with 1 to 2 g. of sodium ammonium phosphate; about 10 c.c. of concentrated ammonia is added and the solution allowed to stand in the cold for at least three hours. The mixture is then *thoroughly* stirred and filtered and the precipitate washed once with cold water while the filtrate is rejected. A hole is made in the filter paper, the magnesium ammonium phosphate washed into the beaker from which it has just been filtered and dissolved in a few c.c. of nitric acid. The solution is again precipitated in exactly the same way as previously indicated. The cold solution is *vigorously* stirred, filtered through a weighed Gooch crucible and washed free from soluble phosphates with cold 10 per cent. ammonia solution. The precipitate is dried, ignited, cooled and weighed as magnesium pyrophosphate—the conversion factor to magnesium oxide being 0·3621.

5. Estimation of Alkalis

0·5 g. of the finely-powdered dry substance is *thoroughly* ground up with about 0·5 g. of ammonium chloride and 3 g. of calcium carbonate in an agate mortar and transferred to a platinum crucible. The mortar is "rinsed out" with another gram of calcium carbonate and the "washings" added to the mixture in the crucible. After well stirring the contents with a glass rod the crucible is heated over a *small* Bunsen flame for about fifteen minutes, the crucible being partly covered by the lid. When all the ammonium salts have volatilised, the lid is placed in position and the lower third of the crucible heated to dull redness for one hour, but the cake must not be fused. The crucible is cooled, the cake transferred to a porcelain basin and the crucible thoroughly rinsed out into the basin with hot distilled water. After a few minutes the cake is gently powdered in the basin with an agate pestle; the mass is then digested with about 80 c.c. of hot water for thirty minutes, filtered, and the residue thoroughly washed with small quantities of hot, distilled water until the washings occupy 120 to 150 c.c. The residue is rejected. (*Cf.* Felspars, p. 17.)

The filtrate is heated to 80° to 90° and 10 c.c. of ammonium carbonate solution (100 g. of ammonium carbonate is dissolved in 100 c.c. of concentrated ammonia (sp. gr. 0·880) and the solution diluted to 500 c.c. with water) added to precipitate the lime. The liquid is filtered and the filtrate retained. A hole is made in the filter paper, the precipitate washed through into the beaker from which it was filtered and redissolved in about 5 c.c. of hydrochloric acid. The solution is boiled, a slight excess of ammonia and ammonium carbonate solution added and the liquid filtered into the vessel containing the first filtrate, the residue being well washed.

The filtrate is first evaporated to dryness in a large platinum or silica dish. The dish is then covered with a clock glass and baked for an hour at 120° in an air oven. After removing the clock glass the dish is ignited at a *dull red* heat until all the ammonium salts have volatilised. The cold residue is moistened with about 3 c.c. of ammonium carbonate solution, in order to precipitate the last traces of lime, and allowed to stand for twelve hours after covering with a clock glass.

The mixture is filtered into a small platinum dish and the precipitate washed with ammonium carbonate solution. The filtrate is evaporated to dryness on a water-bath, but as the liquid tends to spurt during the early stages of the evaporation the dish is covered with a clock glass until the ammonium salts have decomposed, and any liquid adhering to the glass is then washed back into the dish. When dry, the residue in the dish is moistened with a few drops of concentrated

hydrochloric acid, again evaporated to dryness, ignited at a *low red* heat, cooled and weighed. The residue is then washed out with hot water into a small porcelain basin and the platinum dish again ignited and weighed. The difference in weight represents the alkali chlorides. It is advisable to make a blank determination of the alkalis as chlorides in an equivalent weight of ammonium chloride and calcium carbonate and to deduct the amount, if any, from the weight of mixed chlorides.

If the silicate contains appreciable quantities of sulphur the alkali chlorides will be contaminated with sulphates. In such cases the sulphates are converted into chlorides by adding a little barium chloride solution before the final precipitation of the lime.

A few drops of perchloric acid (sp. gr. 1·20) are added to the liquid in the porcelain basin at the rate of 6 c.c. per g. of mixed chlorides and the solution evaporated almost to dryness on a water-bath *in an atmosphere free from ammonia fumes:* 10 c.c. of water is added and the solution again evaporated to dryness. The residue is at once treated with alcohol[1] and immediately filtered through a weighed Gooch crucible which has been previously heated to 120° for one and a half hours. The residue is washed with about 30 c.c. of the alcohol mixture and the crucible and contents dried for one hour at 120° and weighed. The weight of the precipitate represents potassium perchlorate, which is calculated to potassium chloride and deducted from the weight of mixed chlorides to give the weight of sodium chloride. The equivalent amounts of potassium and sodium oxides are then calculated. The conversion factors are: potassium perchlorate to potassium chloride, 0·5381; potassium chloride to potassium oxide, 0·6317; sodium chloride to sodium oxide, 0·5303.

(For details and alternative methods of determining potassium, see Vol. II., p. 399 *et seq.*)

ESTIMATION OF CARBON IN CLAYS

The carbon is estimated by igniting the clay in a current of oxygen and absorbing the carbon dioxide produced in a weighed absorption vessel. If the clay contains carbonates the carbon dioxide obtained from them must be determined by the gravimetric process (p. 12).

A porcelain tube (A, Fig. 1) (2 ft. × 1 in. being a convenient size) is used for the combustion and is heated preferably in an electric tube furnace, B. When volatile carbonaceous matter is present in the clay the forward portion of the tube is packed to within 3 in. of the end

[1] *Alcohol Mixture.* Ninety-seven volumes of absolute alcohol, 3 volumes of water and 0.25 volumes of perchloric acid (sp. gr. 1.20). The solution should be kept in a stoppered glass bottle, containing a few grams of finely-powdered potassium perchlorate. The mixture is well shaken and filtered into a small dry wash bottle immediately before use.

with freshly ignited, wire-form copper oxide which is kept in position by loose plugs of ignited asbestos or small rolls of oxidised copper gauze. The fore end of the tube is fitted with a one hole rubber stopper through which passes one of the side arms of a U-tube, C, filled with granular calcium chloride, the limbs of the U-tube being sealed up after charging. Before the filled tube is used for the first time, a stream of dry carbon dioxide is passed through it for two hours and dry air then drawn through for half an hour to displace the carbon dioxide. The other side arm of the U-tube is connected by thick-walled rubber tubing to a weighed absorption bulb, D, charged with potassium hydroxide solution, made by dissolving two parts of potassium hydroxide in three parts of water, and fitted with a guard tube containing soda lime. The Landsiedle type of bulb, as illustrated, is the most convenient and serviceable. The arms of the U-tube and absorption bulb should be brought into contact with each other under the rubber sleeve to minimise diffusion at the
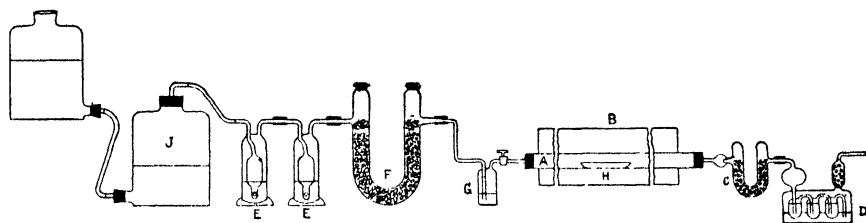
Fig. 1.

joint. The rear end of the combustion tube is connected through another rubber stopper with a purifying and drying train for the removal of carbon dioxide and moisture from the oxygen used in the combustion. An efficient form of train comprises two Muenke's gas washing bottles, E, E, and a large U-tube F (15 in. high × $1\frac{1}{4}$ in. diameter), all connected in series. The bottles are one-third filled with 10 per cent. potassium hydroxide solution, while the rear limb of the U-tube is charged with large granules of soda lime and the fore limb with granular calcium chloride. Between the fore limb of the U-tube and the combustion tube a 50 c.c. gas washing bottle, G, with a glass tap fused to the exit arm, is interposed. Ten c.c. of concentrated sulphuric acid, placed in this bottle, serves to indicate the rate at which gas is passing through the system and the tap provides a means of fine adjustment.

To carry out an estimation about 5 g. of the dry (110°) clay is weighed out into the clay combustion boat, H, and the absorption bulb, D, is also weighed. When not in use the open ends of the bulb are closed by rubber caps but these are always removed before

weighing. The bulb and boat are then placed in their respective positions in the system as shown in the diagram and oxygen is admitted from the aspirator, J, so that about one or two bubbles per second pass through the absorption bulb.

The current through the furnace is turned on and adjusted by an external resistance, so that the furnace reaches a temperature of about 1000° in three-quarters of an hour; the temperature is then maintained at this value by a further adjustment of the resistance.

In about another three-quarters of an hour the carbon will have been completely burnt out of the clay. Owing to the difference in the densities of air and oxygen the oxygen must be swept out of the absorption bulb by a current of pure, dry air before weighing. The simplest way is to detach the oxygen aspirator from the train and replace it by an aspirator containing air; a slow stream of air is then allowed to run through the system for twenty minutes after which the absorption bulb is disconnected, cooled and weighed.

DETERMINATION OF CARBON DIOXIDE IN CLAYS AND CARBONATES

The method of estimating carbon dioxide by the loss in weight, after treating a weighed quantity of the material with acid, is not susceptible of a high degree of accuracy and when the amount of carbon dioxide is small, as in most clays, it is definitely unreliable.

The following adaptation of the method recommended by Fresenius[1] gives excellent results and the whole apparatus (Fig. 2) can be assembled from ordinary laboratory stock. A is a 150 c.c. Claisen flask (or a larger one if the substance froths badly), the neck of which is cut off just above the junction with the side limb; the neck is closed by a rubber stopper through which passes the stem of a small cylindrical separating funnel, B. A small condenser, C, is fixed through another rubber stopper into the auxiliary neck of the flask. This condenser returns the bulk of the steam to the flask on boiling its contents. The side arm of the flask is connected to a drying and purifying train comprising a small gas washing bottle, D, containing concentrated sulphuric acid, a U-tube, E, filled with pumice impregnated with anhydrous copper sulphate, to remove hydrogen sulphide and hydrochloric acid from the gases.

Sixty g. of pumice of the size of peas and free from dust is evaporated to dryness with 200 c.c. of a saturated solution of copper sulphate. The mixture during evaporation is constantly stirred, and when dry heated in an air oven at 140° to 150° for four or five hours.

Another U-tube, F, charged with granular calcium chloride (*cf.* p. 11) serves for the final drying. G is a weighed potash bulb in which

[1] R. Fresenius, *Quantitative Chemical Analysis*, London, 1876, 2, 340.

the carbon dioxide is absorbed. All connections are made with thick-walled rubber tubing (*cf.* p. 11).

Five to 50 g. of the dry clay are made into a thin slip with freshly boiled distilled water and transferred to the flask through a funnel. About 10 c.c. of concentrated hydrochloric acid is then added drop by drop to the mixture from the funnel B, the rate of addition being so adjusted that one to two bubbles of carbon dioxide pass per second through the sulphuric acid in D. When effervescence ceases the contents of the flask are heated over a *small* flame and brought to incipient boiling in about fifteen minutes, while a current of air free from carbon dioxide is slowly aspirated through the system. For this purpose a lime tower, H, is connected to the separating funnel, B, the lower chamber of the lime tower being half filled with 10 per cent. potassium hydroxide solution. The air is forced from an aspirator
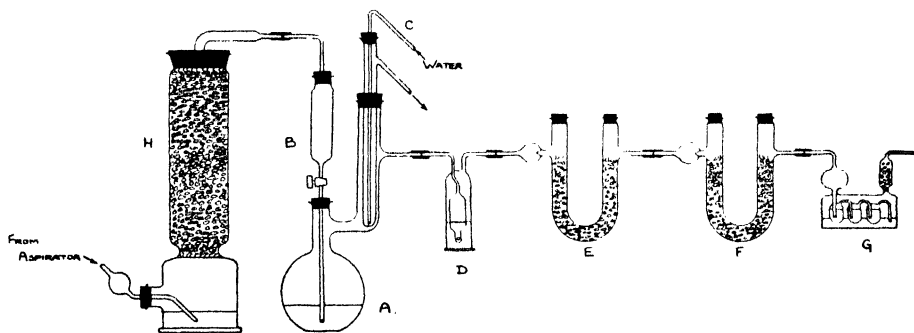
FIG. 2.

through a fine jet dipping under the surface of the potash solution and so on through the system. The rate of flow is conveniently regulated by the tap on the separating funnel. The increase in the weight of G gives directly the amount of carbon dioxide in the weight of clay taken.

ESTIMATION OF SULPHUR IN CLAYS

1. Total Sulphur

One g. of the finely-powdered and dry sample is intimately mixed in a platinum crucible with 3 g. of Eschka's mixture consisting of two parts of light calcined magnesia intimately mixed with one part of anhydrous sodium carbonate, the mixture being kept in a tightly stoppered bottle.

Unless the materials are definitely known to be sulphur-free a blank estimation must be made on 5 g. of the Eschka's mixture and the amount of sulphur present, if any, deducted from that found in the test.

A further 2 g. of the mixture is spread in a layer on the top of the contents of the crucible. In order to protect the mixture from sulphur compounds in the burning gases the open crucible is fitted through a hole in an asbestos board until two-thirds of it projects through the hole. If a spirit burner or an electric crucible furnace is used these precautions are unnecessary, and the crucible is directly heated in a sloping position on a triangle. The asbestos board is fixed in a slanting position between the jaws of a clamp and the lower portion of the crucible *very gradually* heated over a Bunsen burner to drive off any volatile matter without risk of losing sulphur—any escape of sulphur dioxide can be detected by its smell. The rate of heating should be such that in about thirty minutes the lower portion of the crucible is raised to a red heat. The crucible is now covered with the lid and the temperature raised until the whole crucible is red hot, the lid being removed from time to time and the mixture stirred with a stout platinum wire. After about thirty to forty-five minutes' heating at the higher temperature the reaction should be complete, a condition which can be roughly judged by the uniform coloration of the mixture. When cool the more or less powdery mixture is transferred to a 250 c.c. beaker, and the crucible rinsed out with hot distilled water. The mixture and washings are then digested for about thirty minutes with 75 c.c. of hot water, filtered into a 500 c.c. beaker, the residue transferred to the filter paper and washed with hot water until free from alkali. The filtrate and washings should now occupy about 200 c.c.; 4 c.c. of bromine water is added, and enough concentrated hydrochloric acid to make the solution *slightly* acid, the beaker being covered with a clock glass to prevent loss by spurting.

The solution is boiled and when all the carbon dioxide has been expelled the clock glass and sides of the beaker are rinsed down. To the boiling solution a hot $N/1$ solution of barium chloride is added drop by drop from a burette with constant stirring until precipitation is complete, 5 to 10 c.c. being usually ample. The beaker is stood for two hours on a water-bath and, when clear, the supernatant liquid is tested with barium chloride solution to ensure complete precipitation. The solution is subsequently filtered through a fine-grained filter paper; the precipitate transferred to the paper and washed first with 0·1 per cent. hydrochloric acid and then with hot distilled water until free from chlorides. The moist filter paper is placed in a weighed platinum crucible and heated very gradually over a burner with a mushroom head until the paper is completely charred. The final ignition of the residue is carried out at a temperature not exceeding a dull red heat. The residue may be contaminated with some silica derived from the clay, hence it is evaporated to dryness in the crucible

on a sand-bath with a few drops of hydrofluoric and sulphuric acids, again ignited at a dull red heat, cooled and weighed.

2. Sulphur Trioxide

One g. of the dry (110°) clay is fused with 10 to 15 g. of anhydrous sodium carbonate in a platinum crucible, the contents being protected from sulphurous gases in the flame of the burner by the device noted on p. 14. After cooling, the cake is extracted and the crucible thoroughly washed out with hot distilled water to remove all particles from the sides. The cake is digested in a porcelain basin with the washings until it is completely disintegrated. The liquid is filtered and the residue washed with small quantities of hot distilled water until free from alkali. The alkaline filtrate is made *slightly* acid by adding concentrated hydrochloric acid with the usual precautions against loss by spurting. The acid solution is now evaporated to dryness and the silica removed from it as in a clay analysis. The sulphates in the filtrate are subsequently precipitated and weighed as barium sulphate as in the estimation of total sulphur in clays (p. 13). An alternative method is to precipitate the sulphates without removal of the silica and then eliminate the latter from the ignited precipitate by evaporation to dryness with hydrofluoric and sulphuric acids (*cf.* p. 14). There is, however, little to choose between the two methods.

DETERMINATION OF SOLUBLE SALTS IN CLAYS

Certain manufacturing difficulties are caused by the presence of soluble salts in clays and hence it may be necessary to determine their amount and nature.

The soluble salts are determined by boiling 5 g. of the clay with 250 c.c. of distilled water in a hard glass beaker, covered with a clock glass, for about thirty minutes, the water lost by evaporation being made up from time to time. After the clay has settled somewhat the liquid is filtered and the residue well washed with hot distilled water. The filtrate and washings are evaporated to dryness on a water-bath in a weighed dish which has been previously dried at 110°. The residue and dish are then dried at 110° and the increase in weight expressed as a percentage of the clay.

Owing to the finely divided nature of many clays the filtration is frequently a matter of considerable difficulty, as a suspension may be formed which passes through the finest grade of filter paper while some clays take so long to settle that the solid matter appears to be in permanent suspension. The most suitable form of filter is then a Jena glass crucible with a fine grade sintered glass filter disc fused into

the bottom of it. Occasionally it will be found advantageous to remove the coarser particles from the clay suspension by first using a fine grade filter paper and then passing the more or less turbid filtrate through the filter crucible.

Soluble Sulphates

The sulphates are estimated as sulphur trioxide in the soluble salts by moistening the dry residue with a few drops of concentrated hydrochloric acid and then digesting with about 75 c.c. of distilled water. The liquid is filtered, the paper washed free from chlorides and the sulphates in the filtrate precipitated as barium sulphate (1 g. of $BaSO_4$ = 0·3430 g. of SO_3).

The Elimination of Soluble Sulphates from Clays. Soluble sulphates, notably calcium sulphate, are one of the most fertile causes of "scumming" in ceramic wares, and when present in a clay it is necessary to convert them into an insoluble form by the addition of a suitable barium compound—the carbonate or chloride being commonly used.

Theoretically one part of sulphur trioxide present as soluble sulphate requires 2·0465 parts of barium carbonate or 3·0517 parts of barium chloride dihydrate to precipitate it as insoluble barium sulphate. But when barium carbonate is used as the precipitant an excess, say 75 per cent., must be taken so that approximately 3·6 parts of barium carbonate or 3 parts of barium chloride ($BaCl_2$, $2H_2O$) are required for every part of sulphur trioxide present in the soluble salts.

Discrimination between Native and Precipitated Barium Carbonate. For some obscure reason native barium carbonate, witherite, is far less effective for removing the soluble sulphate than the precipitated product, which consequently should always be used.

There is no single test whereby witherite can be conclusively distinguished from the manufactured product, but by a combination of tests it is usually possible to discriminate between them. Some specimens of witherite are greyer in colour than precipitated barium carbonate and on solution in dilute hydrochloric acid leave a larger, denser and darker residue, but much depends upon the source of the mineral and also on its subsequent history during grinding.

Under a microscope precipitated barium carbonate shows crystals of almost uniform size, whereas the crystal fragments from ground witherite are usually larger and more irregularly graded. Nevertheless, by continued wet grinding witherite may be reduced to such a fine state of division that it is indistinguishable under a microscope from the precipitated material, but this contingency is remote in a commercial sample of the ground mineral. Sodium carbonate is commonly used in the preparation of commercial precipitated barium carbonate

and it can be taken for granted that the whole of the precipitant is but rarely removed during subsequent washing. Hence, if the filtrate, obtained from treating a few g. of the sample with hot distilled water, gives an alkaline reaction, this is good evidence that the material is of synthetic origin since witherite on similar treatment gives a neutral filtrate.

II. FELSPARS

The analysis of a felspar is carried out on exactly similar lines to that of a normal silicate, but owing to the relatively high percentage of alkali oxides special precautions have to be taken in the estimation of these constituents.

In the first place, the half gram sample must be ground most thoroughly with the ammonium chloride and calcium carbonate, in fact the grinding cannot be too thorough and, in the second place, after digestion of the sintered mass the residue must be repeatedly washed with small quantities of hot distilled water. Even so, about 2 per cent. of the alkali oxides is still retained by the residue but, whereas with materials containing not more than 5 per cent. of alkali oxides the loss due to this cause is negligible, with felspars and similar minerals this loss introduces an appreciable error in the analysis. To recover the alkalis thus retained, the residue is dried at 110° after washing, detached from the filter paper and again thoroughly ground with another half gram of ammonium chloride. The mixture is transferred to a platinum crucible, the mortar rinsed out with a further gram of calcium carbonate and the whole process of sintering, digestion, filtration and washing repeated. The two filtrates are united and the alkalis recovered from the solution as chlorides in the usual way.

III. BAUXITE

The chief points of difference between the analysis of a clay and of bauxite are as given below.

The finely-powdered sample for analysis is dried at 100°, as at higher temperatures some of the combined water may be lost.

On the other hand the U.S. Bureau of Standards (see Literature, p. 32) recommends that each portion for analysis should be *separately* dried at 140° for two hours, and that every precaution should be taken against access of hygroscopic moisture. The "first" silica is thoroughly washed first with hot 5 per cent. (by volume) hydrochloric acid and then with hot water, while the "second" silica is washed with cool 1 per cent. hydrochloric acid, followed by hot water.

Owing to the high percentage of alumina, the ammonia precipitate is unusually bulky and it is advisable to filter it through a 15 cm.

paper or alternatively to work on 0·5 g. of the material. Special care must be taken during precipitation to keep the solution vigorously stirred, otherwise the precipitate will come down in a gelatinous instead of a granular form and the subsequent washing of it will be unduly prolonged. For the same reason it is necessary to keep the precipitate continuously moist during washing since, if it becomes partially dry, it is almost impossible to wash out the soluble salts completely. As alkali salts tend to be carried down by the ammonia precipitate a triple precipitation is desirable. Great care must be taken to ignite the ammonia precipitate to constant weight at a high temperature.

The percentage of ferric oxide in many bauxites is too high for the colorimetric method of estimation, and the volumetric method (p. 6) must be used. The titration being made in duplicate on 50 c.c. of the stock solution.

Usually the titanium dioxide can be estimated colorimetrically, but in certain bauxites, notably those of Indian origin, the amount is so largely in excess of 4 per cent. that a gravimetric method must be used.[1]

Calcined Alumina and Alundum

Alundum is only superficially attacked by molten alkali carbonates and calcined alumina more or less slowly; hence, when analysing such materials it is advisable to open up the sample by fusing 1 g. of it with 10 to 15 g. of potassium bisulphate until a clear melt is obtained.

The cold cake is extracted, dissolved in water to which 10 c.c. of concentrated sulphuric acid has been added, filtered and the insoluble residue washed free from sulphates. The residue is then ignited, fused with a little sodium carbonate, and the cake, after extraction with water, acidified with 10 c.c. of concentrated sulphuric acid. The solution is evaporated as far as possible on a water-bath, then transferred to a sand-bath and the evaporation continued until the sulphuric acid begins to fume strongly. After cooling the mass is digested with water, filtered, and the residue washed free from sulphates. The residue is ignited and the silica in it estimated by evaporation with hydrofluoric and sulphuric acids in the usual way.

The two filtrates are combined and the alumina in them is estimated as described under the analysis of bauxite, and the other basic oxides as in a clay analysis.

[1] See J. W. Mellor, *Quantitative Inorganic Analysis*, London, 1913, p. 209; W. W. Scott, *Standard Methods of Chemical Analysis*, New York, 1927, p. 542.

IV. LIMESTONES, DOLOMITES, MAGNESITES AND PRODUCTS MANUFACTURED THEREFROM

The analysis of these materials does not differ in principle from that of a normal clay, but the high percentage of alkaline earth oxides introduces complications, *e.g.*, the ammonia precipitate is apt to be contaminated with both lime and magnesia, and in particular the separation of calcium from magnesium offers considerable difficulty.

A large amount of work has been done on the separation of calcium and magnesium and the details and conclusions published by different analysts are not infrequently at complete variance one with another. In fact, no one process has as yet won universal acceptance; the method suggested below has been found to give satisfactory results and it can be recommended provided the experimental details are strictly observed.

Loss on Ignition. The dried (110°) sample should be heated gradually, as if the carbonates are decomposed too rapidly solid particles tend to be carried off in the stream of carbon dioxide. It is essential that the ignition should be repeated until a constant weight is obtained, otherwise the reported loss will be too low owing to the incomplete decomposition of the carbonates. The hygroscopic properties of calcium and magnesium oxides should be borne in mind when cooling and weighing the ignited sample.

The percentage loss on ignition minus the percentage of carbon dioxide gives the loss due to combined water, organic matter and sulphurous gases from sulphates. The percentage of carbon dioxide, if required, is determined by the gravimetric process (p. 12) or by the loss in weight after treatment with acid in one of the many forms of carbon dioxide apparatus.

Opening up the Sample. Owing to the high percentage of acid-soluble material in the natural carbonates, various methods have been proposed whereby the fusion with sodium carbonate need not be carried out in its entirety. It is doubtful if any time is gained by these methods, as in the general case, after treatment with acid, a siliceous residue is left which must be subsequently decomposed by fusion with sodium carbonate. The process here recommended is to take 1 g. of the dry, *unignited* material and fuse it in the usual way with 10 to 15 g. of anhydrous sodium carbonate.

In the case of manufactured products such as magnesite bricks, the fusion should be continued with constant agitation for at least forty-five minutes, as magnesite bricks are particularly difficult to decompose.

1. Silica

Where not more than 5 or 6 per cent. of silica is present, only one evaporation to dryness is necessary. On evaporation to dryness of the acid solution obtained from materials rich in magnesium oxide, more or less of the magnesium chloride is hydrolysed to a sparingly soluble basic chloride, part of which on filtration remains behind with the silica. Hence, after evaporation and the subsequent baking at 110° the dry residue should be moistened with an excess of concentrated hydrochloric acid and digested on a water-bath for a few minutes before dilution.

2. The Ammonia Precipitate

The filtrate from the silica is diluted to about 300 c.c., 10 g. of ammonium chloride added, followed by a few c.c. of bromine water to ensure precipitation of any manganese present. The solution is heated to 80° to 90°, a *slight* excess of ammonia added and the heating continued for another five minutes. Prolonged boiling, a large excess of ammonia and very concentrated solutions must be avoided, otherwise the ammonia precipitate will be contaminated with much lime and magnesia.

The same precautions must be observed in the reprecipitation, but the amount of ammonium chloride can be reduced to 7 g. When the ammonia precipitate does not exceed about 5 per cent. it is unnecessary to evaporate the filtrate to small bulk and again make ammoniacal after the second precipitation, but in such cases it is advisable to boil off the excess of ammonia before the second filtration.

3. Lime

The lime is determined in the usual way by precipitation with ammonium oxalate. To minimise the simultaneous precipitation of magnesia the solution should occupy not less than 300 c.c.; not more than 2 g. of the precipitant should be added followed by a *slight* excess of ammonia and vigorous heating should be avoided. After the solution has stood for two hours on a water-bath the precipitate must be filtered off, redissolved and again precipitated, observing all the above precautions. If there is any reason to suspect that the precipitate is still contaminated with magnesia a third precipitation must be made. The accuracy of the result can always be confirmed by converting the calcium oxide into sulphate as indicated under the estimation of fluorine (p. 27), though it is advisable to use 25 per cent. sulphuric acid instead of the concentrated acid (1 g. CaO = 2·4278(6) g. $CaSO_4$).

4. Magnesia

In materials with a high proportion of magnesia the precipitation is best made in a volume of about 300 c.c.; 5 g. of microcosmic salt is added, the solution is boiled for a few minutes and then made alkaline with 10 to 15 c.c. of concentrated ammonia. The subsequent procedure is now as given under the estimation of magnesia in clays (p. 8). If too much ammonia or microcosmic salt is used the precipitate will be contaminated with the latter, which is very difficult to remove by washing. The bulky precipitate naturally requires a very thorough washing with cold 10 per cent. ammonia solution after the second precipitation and it should be ignited throughout to a temperature of not less than 800°.

V. BARYTES

This mineral is so cheap that it is very rarely adulterated and consequently the impurities are those of natural origin.

The barium sulphate is usually associated with varying amounts of silica, aluminium and iron oxides, calcium and magnesium carbonates and water, either free or combined with gypsum or clay. Fluorides (as fluorspar) are not at all uncommon and traces of copper and lead sulphides are sometimes present.

Loss on Ignition (see Clays, p. 2). If necessary, a separate estimation of the carbon dioxide can be made, preferably by the gravimetric process (p. 12).

1. Silica

The residue left after ignition, or a fresh gram of the dry sample, is fused with 10 to 15 g. of anhydrous sodium carbonate in a platinum crucible until the melt is in a state of quiet fusion. When cool, the cake is detached from the crucible and the latter thoroughly rinsed out into a porcelain evaporating basin with hot distilled water until all adhering particles have been removed. The cake is then completely disintegrated by digesting it in the basin with the washings from the crucible. The liquid is filtered and the residue washed free from alkali with hot distilled water. The silica is distributed between the filtrate and the residue.

Removal of the Insoluble Silica. The filter paper containing the residue is punctured at the apex and its contents washed as completely as possible into an evaporating basin. The solution is acidified with 10 to 15 c.c. of concentrated hydrochloric acid with the usual precautions against loss by spurting. When active effervescence has ceased, the filter paper is washed with hot dilute hydrochloric acid, followed

by hot distilled water until it is free from chlorides. The filter paper is retained for subsequent ignition. The silica is recovered from the acid solution and washings by two evaporations to dryness and bakings at 110° with an intervening filtration as in a clay analysis: the filtrate is reserved for the estimation of barium oxide.

Removal of the Soluble Silica. The alkaline filtrate from the digestion of the cake is acidified with hydrochloric acid and the silica recovered from it as above.

The filter papers containing the two silica precipitates together with the paper used in the initial filtration of the disintegrated cake are ignited in a platinum crucible and the silica estimated by the loss in weight after evaporation of the ignited residue with hydrofluoric and sulphuric acids.

The crucible and final residue are retained for the subsequent ignition of the ammonia precipitate.

2. Barium Oxide

The filtrate from the insoluble silica is heated to boiling and a hot 10 per cent. solution of sulphuric acid added drop by drop with constant stirring from a burette until in slight excess (about 25 c.c. is required). The precipitate and mother liquor are digested for two hours on a water-bath, the liquid after settling being tested with a few more drops of sulphuric acid to ensure complete precipitation. The precipitate is filtered through an ignited and weighed Gooch crucible *thickly* packed with asbestos, washed free from chlorides and sulphates with hot distilled water, ignited, cooled and weighed.

3. Aluminium, Iron, Calcium and Magnesium Oxides

The filtrate from the barium oxide estimation is added to the filtrate left after removal of the soluble silica, and the aluminium, iron, calcium and magnesium oxides determined in the combined solution by the usual processes (*cf.* pp. 4-8).

Sulphur Trioxide, see "Estimation of Sulphur Trioxide in Clays," p. 15.

VI. ZIRCONIUM MINERALS AND MANUFACTURED PRODUCTS

The following modifications of a typical clay analysis are necessary when working with materials containing zirconium. When the percentage of zirconium oxide is high it is advisable to carry out the analysis on half a gram of the material.

1. Silica

Frequently it is most difficult to "open up" a zirconium compound and the sample for analysis should be ground to a very fine powder; 0·5 g. of the dry (110°) powder is *cautiously* fused in a platinum crucible with 5 to 8 g. of sodium bisulphate and the heat gradually increased until the melt becomes quite viscous. When cold the cake is extracted and digested at a low temperature (40° to 50°) with about 100 c.c. of 10 per cent. sulphuric acid, the insoluble silica filtered off, washed free from sulphates, ignited and weighed; the filtrate is retained for the estimation of basic oxides. If the ignited silica is not colourless it should be again fused with a little sodium bisulphate and the process of extraction and filtration repeated. The silica is estimated by the loss in weight after treatment with hydrofluoric and sulphuric acids. As the silica holds back some of the zirconium very tenaciously, the residue in the crucible after the acid treatment is fused with sodium bisulphate, the cold cake taken up in a little dilute sulphuric acid and the solution added to the filtrate from the silica.

The combined filtrates from the silica are warmed from 40° to 50°, and hydrogen sulphide passed through the solution until cold to precipitate any platinum dissolved from the crucible by the action of the molten bisulphate. After filtering off any precipitate the solution is *gently* boiled to expel hydrogen sulphide and finally a few c.c. of nitric acid is added to oxidise the iron. Prolonged and vigorous boiling of the solution must be avoided, otherwise partial hydrolysis of the zirconium sulphate may result. An alternative method is to remove the bulk of the hydrogen sulphide by a stream of hydrogen and then bring the solution to the boiling-point for a few minutes.

The mixed oxides of aluminium, iron, titanium and zirconium are then precipitated in the usual way from the solution (p. 4).

2. Zirconium Oxide

Fifty c.c. of the stock solution used for the colorimetric estimation of iron and titanium is taken and diluted to 175 c.c. with distilled water; 10 c.c. of 20 vol. hydrogen peroxide is then added followed by 20 c.c. of sulphuric acid (sp. gr. 1·84). The solution now contains approximately 20 per cent. by weight of sulphuric acid. The hydrogen peroxide prevents the subsequent precipitation of titanium as phosphate. The solution is warmed to 40° to 50° and 3 to 4 g. of secondary ammonium phosphate [$(NH_4)_2HPO_4$] added. After keeping the solution warm for two hours as much as possible of the supernatant liquid is decanted through a filter paper, the precipitate is transferred to the paper and washed with cold 5 per cent. ammonium

nitrate solution until free from sulphates. The paper is ignited very carefully in a partially covered platinum crucible over a low flame until all the carbon is burnt off and then the crucible and contents are strongly heated to constant weight.

The weight of the precipitate multiplied by 0·4632 gives the corresponding amount of "zirconium" oxide.

Any hafnium present in the material will be precipitated as phosphate together with the zirconium. In view of the large difference in the atomic weights of hafnium and zirconium (178·6 and 91·2) subsequent conversion of the mixed phosphates into oxides has been recommended. The weighed phosphates are fused with sodium carbonate, the extracted cake digested with water and the insoluble sodium hafnate and zirconate filtered off. The residue after washing free from alkali is dissolved in hydrochloric acid and the mixed oxides precipitated by ammonia. From the respective weights of mixed phosphates and mixed oxides, the individual weights of hafnium and zirconium oxides can be calculated. However, in most technical analyses this procedure is unnecessary and it is sufficient to use the conversion factor given above and report as zirconium oxide.

VII. CHROMITE

The compound is broken down by fusion with sodium peroxide whereby the chromium sesquioxide is oxidised to sodium chromate. A measured excess of a standard ferrous iron solution is added to an aliquot portion of the acidified chromate solution and the unoxidised ferrous iron estimated by titration with a standard solution of potassium permanganate. (*Cf.* Vol. II., pp. 12, 33, 72.)

0·5 g. of the dry (110°) finely-powdered ore is weighed out in a nickel crucible and intimately mixed with about 8 to 10 times its weight of "reagent" sodium peroxide. The crucible is then heated over the tip of a Bunsen flame until its contents are in a state of quiet fusion. When cool the crucible is placed in a 400 c.c. beaker, the beaker covered with a clock glass and about 100 c.c. of water introduced from a pipette through the lip of the beaker. After active effervescence has ceased the under side of the clock glass is rinsed into the beaker, the crucible removed with a pair of gun-metal (not iron) tongs and thoroughly washed both inside and out with hot distilled water. The solution and washings, which should now occupy about 150 to 200 c.c., are *well* boiled and then set aside for a few minutes to settle. The solution is filtered through a Gooch crucible, the residue transferred from the beaker to the crucible and washed with hot distilled water until free from alkali.

1. Estimation of Chromium Sesquioxide.

The filtrate and washings, when cold, are made up to 500 c.c. in a graduated flask and the solution well shaken. Fifty c.c. of this solution is pipetted into a beaker and acidified with about 50 c.c. of sulphuric acid (1 in 4), 25 c.c. of approximately $N/10$ ferrous ammonium sulphate solution is added and the amount of unoxidised iron estimated by titration with $N/10$ potassium permanganate solution.

The ferrous ammonium sulphate solution is made by dissolving about 10 g. of the finely-powdered salt in 200 c.c. of cold distilled water; the solution is acidified with 10 c.c. of concentrated sulphuric acid, diluted to 250 c.c., and its exact titre determined by acidifying 25 c.c. with 50 c.c. of 1 in 4 sulphuric acid and titrating with standard permanganate solution.

Every gram of ferrous iron oxidised represents 0·4537(3) g. of chromium sesquioxide in the chromite.

2. Ferrous Oxide

The washed residue left on the Gooch crucible after filtration of the sodium chromate is *at once* dissolved in warm (1 in 4) sulphuric acid. If allowed to become dry the residue does not dissolve so readily; incomplete solution of the residue indicates that the ore has not been wholly decomposed during the fusion. The solution thus obtained is reduced with zinc or magnesium and titrated with $N/10$ potassium permanganate solution. The result is usually calculated to FeO.

3. Complete Analysis

0·5 g. of the ore is intimately ground in an agate mortar with 10 g. of sodium carbonate and 0·5 g. of potassium nitrate. The mixture is transferred to a platinum crucible and fused at a bright red heat for at least one hour. The cake is extracted with water acidified with sulphuric acid and the silica removed from it as in the analysis of alundum. The filtrate is treated with a slight excess of sodium peroxide which precipitates the iron and reoxidises to chromate any chromium which may have become reduced during the evaporation for silica. The ferric hydroxide is filtered off, redissolved, reprecipitated, and the weight of the ignited oxide calculated to FeO.

The filtrate and washings from the ferric hydroxide contain the chromium, aluminium, calcium and magnesium oxides. The aluminium oxide is determined by acidifying the filtrate with sulphuric acid followed by precipitation with ammonia. The residual solution is made up to 500 c.c. and the chromium sesquioxide estimated in an aliquot part of it by the volumetric method described above, and

the calcium and magnesium oxides by the standard methods in another portion of the solution—200 or 300 c.c. being a convenient volume to take.

VIII. FLUORSPAR, CRYOLITE AND FLUORIDES

No thoroughly reliable process for the analysis of fluorides has as yet been worked out, but the following method based on that originally proposed by Berzelius and Rose gives, with care and practice, reasonably accurate results.

Loss on Ignition. One gram of the dry (110°) powdered fluorspar is heated in a platinum crucible to a *dull red* heat for twenty to thirty minutes, cooled and weighed. Alkali fluorides volatilise at a comparatively low temperature, hence no significance can be attached to a determination of their loss on ignition. Calcium fluoride is, however, more stable towards heat, though losses have been reported at higher temperatures.

1. Separation of Silica and Bases

One gram of the dry (110°) powdered mineral is mixed in a platinum crucible with about 12 g. of anhydrous sodium carbonate and the mixture fused at a low temperature. When cool, the cake is detached from the crucible, placed in an evaporating dish, and all adhering particles removed from the interior of the crucible by rinsing it into the dish with hot distilled water.

The cake is then digested with the washings on a water-bath until it is completely disintegrated. The mixture is filtered (filtrate A) and the residue washed with hot distilled water until free from alkali. A hole is poked through the filter paper and the residue washed into an evaporating dish with hot 10 per cent. hydrochloric acid. The paper is washed free from chlorides and is reserved, together with the acid solution and washings (solution X), for the estimation of bases and silica.

Filtrate A and washings contain the fluorine as alkali fluoride, the remainder of the silica, and alumina, if present. Ten grams of solid ammonium carbonate is added to it and the mixture is digested for twelve hours at 40° to 50° whereby the alumina and a further quantity of silica are precipitated. The liquid is filtered (filtrate B) and the precipitate well washed with 10 per cent. ammonium carbonate solution.

The precipitate is dissolved off the filter paper with hot hydrochloric acid solution and the paper washed free from chlorides. The paper is retained and the acid solution and washings added to solution X.

Filtrate B still contains some silica. It is transferred to an evaporating dish, covered with a clock glass and heated on a water-

bath until the ammonium carbonate is all decomposed. The under side of the clock glass is rinsed into the dish and the solution evaporated to dryness. The residue is then digested with a little water and cooled. Two drops of phenolphthalein are added to the solution and 2*N* nitric acid run in from a burette until the colour of the indicator is just discharged. The solution is heated and then boiled for several minutes when the red colour reappears; the solution is cooled, neutralised, and again boiled, this process being repeated until the final addition of 1 to 1·5 c.c. of the acid produces a permanent discharge of colour. Ten c.c. of Seemann's solution (see below) is added to the neutralised solution and the mixture evaporated until the smell of ammonia disappears. The precipitate consisting of traces of silica and mercuric oxide is filtered off (filtrate C) and washed with water. The filter paper is retained.

Seemann's Solution. Mercuric oxide is precipitated by adding a solution of sodium hydroxide to a hot saturated solution of mercuric chloride. The precipitate is washed with hot water until a portion of it volatilises on platinum foil without residue. About 20 g. of moist mercuric oxide, freshly prepared in the above way, is dissolved to saturation in a litre of Schaffgotsch's solution, made by dissolving 230 g. of ammonium carbonate in 180 c.c. of ammonia solution (sp. gr. 0·92) and diluting to a litre.

2. Estimation of Fluorine

Filtrate C and washings are just neutralised with nitric acid, care being taken to avoid losses by spurting, and sodium carbonate solution is then added until the solution is distinctly alkaline. A large excess of an aqueous solution of calcium chloride is added and the mixture boiled. Calcium fluoride and carbonate are precipitated; after settling, the clear liquid is tested with a few drops of sodium carbonate to ensure the presence of excess of calcium chloride. The precipitate is filtered off, washed with hot water, dried and ignited slowly to faint redness in a platinum basin. The basin is covered with a watch glass and dilute acetic acid in excess of that needed to dissolve the calcium carbonate, introduced through a pipette. The covered basin is heated on a water-bath until effervesence ceases. The watch glass is removed, rinsed into the basin and the mixture evaporated to dryness. Next the residue is digested with water, slightly acidulated with acetic acid, then filtered, washed and ignited as before, the filtrate being retained. To remove the last traces of soluble calcium compounds the digestion with weak acetic acid solution should be repeated, the filtrate again being retained.

Frequently the last traces of silica escape precipitation by the Seemann's solution, hence these two filtrates are combined and the

silica in them estimated by evaporation to dryness with hydrochloric acid. The silica thus obtained is added to that separated from solution X.

After the second digestion the filter paper and residue of calcium fluoride are ignited gently to faint redness in a platinum crucible, cooled and weighed.

It is advisable to confirm the result by converting the fluoride into sulphate. The crucible is half filled with concentrated sulphuric acid, placed *eccentrically* on a sand-bath and the mixture slowly evaporated to complete dryness. After cleaning the outside of the crucible, it is ignited at a dull red heat, cooled and weighed. The increase in weight multiplied by 1·3450 gives the corresponding amount of calcium fluoride, or, multiplied by 0·6545, the equivalent quantity of fluorine.

An alternative procedure[1] is to neutralise the alkaline solution of the fluoride (Filtrate C) with nitric acid, using methyl red as indicator, until on repeated boiling and cooling the yellow colour does not return. One or two drops of nitric acid are added to the solution, followed by a slight excess of calcium chloride solution; the solution is then heated nearly to boiling and stood overnight before filtering through a *membrane* filter. The filter is dried for one hour in a vacuum desiccator; the precipitate is then transferred to a crucible and heated for thirty to forty minutes at about 500°. Since the precipitation is made in faintly acid solution calcium carbonate is not simultaneously precipitated with the fluoride.

3. Determination of Silica and Bases

The three filter papers obtained in the silica separations are ignited in a platinum crucible during which process the mercuric oxide, derived from the Seemann's solution, is volatilised. The ashes are added to solution X, followed by 10 c.c. of concentrated hydrochloric acid and the silica and bases determined in the mixture as in a typical clay analysis (pp. 2-8).

W. T. Schienk and W. H. Ode[2] have shown that silica can be accurately determined in the presence of fluorspar as follows:—0·5 g. of the finely ground sample is digested in a hard glass beaker with 15 c.c. of 20 per cent. perchloric acid, which has been previously saturated with boric acid at 50°, until fumes of perchloric acid have been evolved for about five minutes. A few c.c. of water are added and the fuming repeated for another five minutes, 75 c.c. of water is added, the solution heated and the insoluble residue filtered off. The filter paper and residue are first washed with dilute perchloric acid and finally with hot water until the filtrate gives no precipitate with ammonium oxalate. The insoluble residue is ignited and the silica in it estimated by the loss in weight

[1] G. G. Kandilarow, *Ber.*, 1928, 61 **B.**, 1667.
[2] *Ind. Eng. Chem.*, Anal. Ed., 1929, I., 201.

after evaporation with hydrofluoric acid. During the treatment with perchloric acid the fluorine is eliminated as boron fluoride.

4. Alkalis

The alkalis are estimated as in a standard silicate analysis (p. 9).

If the bases are calculated as oxides, a deduction must be made from the total analysis of 0·4210(5) g. of oxygen for every gram of fluorine present since a larger or smaller proportion of the bases, according to the nature of the material under analysis, are present as fluorides and not as oxides. The analysis is consequently reported as: "total—per cent. less 0·4210(5)p per cent. of oxygen corresponding to p per cent. of fluorine."

IX. THE ANALYSIS OF GLAZES

It is impossible to give a general scheme for the analysis of glazes, as to a large extent each glaze requires its own method. In every case the analysis of an unknown glaze must be preceded by a careful qualitative examination and the subsequent procedure in the quantitative analysis is conditioned by the constituents found to be present. For a detailed treatment of the various separations involved in any particular analysis reference must be made to the section on analysis of Glass, pp. 215-283, or to one or other of the more advanced treatises on quantitative analysis (see Literature, p. 32).

As an indication of the type of procedure to be adopted, details for the analysis of standard leadless and lead glazes are given here.

The composition of these two glazes approximates to:—

	SiO_2	PbO	Al_2O_3	CaO	Na_2O	K_2O	B_2O_3	
Leadless Glaze .	52·72	...	14·40	8·07	2·36	5·42	17·02	per cent.
Lead Glaze . .	49·30	24·43	6·98	4·60	5·09	...	9·58	„

The standard silicate analysis is thus complicated by the presence of boric oxide in both glazes and by lead oxide in the lead glaze, hence it is modified in the following respects:—

Loss on Ignition. Since the majority of glazes are made by fritting the materials together, it is unnecessary to determine the loss on ignition. On the contrary, if boric oxide or fluorides are present, some may be lost by volatilisation during ignition; hence it is important not to calcine the sample prior to analysis.

Silica. In the isolation of the silica, only part of the boric oxide is volatilised during the two evaporations to dryness and the remainder is precipitated with the aluminium and iron, thus giving high results.

Consequently, 20 c.c. of *pure* methyl alcohol is added to the solution before each evaporation to dryness which ensures the elimination of the whole of the boric oxide as volatile methyl borate. (*Cf.* Glass, p. 245.)

1. Lead Oxide

The filtrate from the silica is diluted to 250 to 300 c.c., warmed to 80° to 90° and ammonia added drop by drop until a faint permanent precipitate results. The solution is cleared by the addition of a few drops of concentrated hydrochloric acid (sp. gr. 1·16) followed by 3 c.c. of the acid for every 100 c.c. of solution. Whenever Group II metals are present, it is important to adjust the acidity of the solution to this limit, as with greater acidity some of these metals are incompletely precipitated and with lower acidity metals of other groups, notably zinc, tend to be separated. After again warming up the solution, if necessary, a slow stream of hydrogen sulphide is passed through it until cold. The solution is next filtered and the precipitated lead sulphide washed thoroughly with cold distilled water which has been previously saturated with hydrogen sulphide. The precipitate is dissolved off the filter paper by a solution (40 per cent. by volume) of nitric acid containing a few drops of bromine and the filter paper subsequently washed well with hot distilled water. Sulphur may separate during the solution of the lead sulphide as a darkish, plastic residue which is discarded after washing. Eight c.c. of concentrated sulphuric acid is added to the filtrate and washings and the solution is evaporated in a fume cupboard on a hot-plate or sand-bath until its volume is reduced to 3 c.c. After cooling, 100 c.c. of cold water is added and the solution is filtered through an ignited and weighed Gooch crucible. The precipitate is washed with approximately $N/1$ sulphuric acid and finally with alcohol until free from sulphuric acid. The crucible and contents are ignited to a dull red heat, cooled and weighed and to the weight of lead sulphate thus obtained a correction of +0·0006 g. is made, this being the solubility of the salt in 100 c.c. of $N/1$ sulphuric acid.

2. The Ammonia Precipitate

The filtrate from the lead sulphide is boiled until all the hydrogen sulphide is expelled and the solution then oxidised by the addition of a few c.c. of nitric acid. The course of the analysis now follows that of a typical clay.

3. Boric Oxide

The consensus of opinion seems to be that the only accurate and reliable method of estimating boric oxide is by the distillation process which is both difficult and laborious and ill-adapted for technical work

The modification of Wherry's process, due to Sullivan and Taylor, described in the section on Glass, p. 252, gives results quickly and sufficiently accurate for most analytical purposes.

For the determination of the very varied constituents in glazes the methods used for analysis of glasses of corresponding composition are available. (*Cf.* Glass, pp. 215-283.)

The "Government Test" for the Solubility of Lead Frits and Glazes

A few g. of the finely-powdered frit or glaze is dried at 110°, or if the glaze is supplied in "slop" form it is thoroughly shaken and without allowing the mixture to settle a portion is poured into a basin and evaporated to dryness on a water-bath. As the glaze is not usually homogeneous after evaporation the resulting powder is intimately mixed and finally dried at 110°, 0·5 g. of the dry material is transferred to a 500 c.c. Stohmann flask which is then filled up to the mark on the neck with 0·25 per cent. hydrochloric acid (weight/weight). The flask is closed by a rubber stopper and the mixture continuously agitated for one hour at room temperature in a shaker—the Wagner pattern can be recommended. The flask is then set aside for another hour, after which the solution is filtered through a *dry* paper, the first 10 c.c. being rejected. As some glazes do not filter satisfactorily through filter paper, it may be necessary to adopt the method mentioned under "The Determination of Soluble Salts in Clays" (p. 15). 450 c.c. of the clear filtrate is taken and the lead in solution precipitated by hydrogen sulphide and estimated as lead sulphate by exactly the same process as that given under "The Analysis of Glazes" (p. 30). The lead sulphate is calculated to lead monoxide, which is reported as a percentage on the dry weight of the glaze.

If there is any reason to suspect that silica from the glaze is passing into solution through the action of the hydrochloric acid, the 450 c.c. of filtrate is first evaporated to dryness and, after moistening the residue with dilute hydrochloric acid, the silica is filtered off and washed free from chlorides. The filtrate and washings are diluted to about 150 c.c. and acidified with 3 c.c. of concentrated hydrochloric acid. The lead is then removed from the solution as indicated above. However, only in exceptional cases is it necessary to adopt this procedure.

The lead solubility test is invariably run in duplicate and the mean value taken since the experimental error in an individual estimation may put the soluble "lead" in a glaze above or below the permissible limit to which the glaze should conform. A low solubility glaze when subjected to the above test must not *yield* more than 5 per cent. of lead monoxide on its dry weight.

Total "Lead."—For a glaze to be classed as "leadless" it must not *contain* more than 1 per cent. of lead monoxide on its dry weight. The lead monoxide is estimated in the glaze by the method given on p. 30.

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CLAYS, CERAMIC PRODUCTS AND REFRACTORIES—PHYSICAL EXAMINATION

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I.—THE EXAMINATION OF RAW CLAYS

THE clay technologist deals largely with arrested physical and chemical changes. The conditions governing the arrest of the fusions, solutions and crystallisations in ceramic ware during firing determine, above all, the characteristics of the finished article. Some of these conditions are external, others are peculiar to clays. The aim of the physical examination of clays for industrial use is to define all their physical characteristics, and most particularly, those which affect the essential properties of the ceramic product. Thus while the results of certain tests, such as mechanical analysis, drying and firing shrinkages, mechanical strength and refractoriness are of general value, other information is only required for specific purposes; a china manufacturer takes great interest in the colour of his clay after firing, a brick manufacturer in the presence of calcium carbonate nodules in his raw material, while the maker of electrical porcelain displays the keenest interest in the last traces of porosity in his ware and its electrical resistivity; and so on throughout the whole diverse range of ceramic manufactures. Sufficient has been said to give the reader a proper perspective in looking over the field of ceramic testing; in some cases, alternative tests will be found to suit varying requirements. Generally, the clay-worker should bring an intimate practical acquaintance with his own processes to bear on the selection of all those tests which give data bearing on the essentials of his processes and products.

The variety in the chemical constituents of clays as shown in the chemical section is reflected in their physically heterogeneous nature. The great bulk of the world's clays are of secondary, sedimentary origin, and contain the finest debris of the decay of rocks of plutonic origin, together with more or less organic matter and minerals formed subsequently to the deposition of the clay. An amorphous, or crypto-

crystalline, compound of alumina, silica and water, named clayite by J. W. Mellor, is considered to be a characteristic constituent of all clays, and either this, or the crystalline kaolinite of the same formula, $Al_2O_3 . 2SiO_2 . 2H_2O$, is present in all clays and tends largely to predominate in those of highest quality for ceramic purposes. It is a straightforward application of petrography to isolate the constituent minerals in the coarser part of a so-called clay—that is, in that part whose particles exceed about 0·1 mm. in diameter—but it becomes increasingly difficult to make a *mineral* separation of the particles much below this size. As the great bulk of many typical clays consists of colloidal matter less than 0·2 μ in diameter, it will be seen that the mineral analysis at present assumes a secondary importance. In addition to this, it is customary in the manufacture of all the higher grades of ceramic ware to sift out all material which will not pass a mesh of about 120 to the linear in. (an aperture of 0·107 mm.): consequently, the coarse material is of no consequence, except as a loss, or in so far as it gives an indication of the quality of the clay. In high-grade clays the coarse material consists mainly of quartz grains, micaceous plates and, in black ball clays, lignite. If pyrites or marcasite is abundant, it gives a *prima facie* indication of the unreliability of the clay. For those wishing to follow up the mineralogical examination of the coarser fractions, reference may be made to J. W. Evans,[1] A. Johannsen[2] and A. Holmes.[3]

Examination of Material in the Rough State

The examination of a clay, as received from the quarry or mine, begins naturally with the general physical characteristics of the lump material. First, note whether the clay is soft and plastic when moistened or hard and shaly, also, if necessary, the degree to which induration has proceeded; this may be judged by breaking pieces with the hands or a hammer. Fossils, fossil-markings, ripple-marks, etc., may give valuable indications as to the origin and general characteristics of the material. Hard clays and shales often break down if left exposed to the atmosphere (weathering) for a period which may vary from a few hours to as many years. The process of disintegration is assisted by grinding, or grinding followed by boiling or steaming. If the material is a very hard shale, its properties will not depend so much on the primary, fine-grained structure of the rock as on the degree of grinding, natural weaknesses due to bedding-planes or pressure, and lack of uniformity. In general, the preliminary qualitative examination should include observation and note of colour,

[1] *The Determination of Minerals under the Microscope*, London, 1928.
[2] *Manual of Petrographic Methods*, New York, 1918.
[3] *Petrographic Methods*, London, 1921 and 1923 (Part I.).

hardness, fracture, if any, macroscopic impurities including organic matter, uniformity, behaviour in crushing; this should be followed, with allowance for weathering where necessary and re-examination of the weathered material, by working the clay up with water and noting the behaviour in pugging, forcing through dies and cutting with a taut wire.

Firing Trials on the Rough Clay

Valuable information is often obtained by subjecting a few lumps of the raw clay, as received, to the ordinary firing process, or by giving it a similar treatment in a laboratory furnace. The results often indicate the nature of erratic impurities (*e.g.* chalcopyrite in fireclay for sanitary ware), and sudden changes in the firing properties in adjacent layers in the original deposit. The test-pieces may be glazed and re-fired to the normal firing temperature of the works glost ovens, when further useful information may accrue. No final judgment of the value of a clay is, however, advisable until tests have been carried out with normally prepared material, except when the clay is known to be merely a slight variant on one normally used and already thoroughly tested.

Substitution of Clays in High-grade Ware

Where, as frequently happens, a new clay is being examined as a possible alternative to a clay already used alone or in conjunction with other ceramic materials, the foregoing and a selection of the following tests may be used as a rapid means of classifying the clay and eliminating one which is definitely unsuitable. No final judgment can, however, be passed on the suitability of a substitute in the higher grades of ware (*e.g.* fine earthenware or bone china) until the clay has been put through the ordinary manufacturing processes in substitution for the clay normally used. Various articles and test-pieces should be made up and subjected to the tests for finished ware, and the results compared with the most stringent requirements of the ware and the normal results obtained in ordinary practice. A valuable semi-works trial may be put through in the laboratory, but it is advisable to depart as little as possible from the works processes: in particular, final trials are best fired in the commercial ovens and kilns.

True Specific Gravity

This method is suitable for all ceramic materials, except that some such liquid as paraffin oil is used instead of water in the case of clays. Paraffin will also be suitable for materials which are somewhat soluble in water (*e.g.* borax frits). Samples should, in general, be thoroughly dried at 110° before use. The

following specification of the American Ceramic Society[1] relates particularly to fired goods. At least two pieces should be taken from different parts and not have a greater specific surface than the original piece. The samples are together crushed between hardened steel surfaces, if necessary, and ground in an agate mortar to pass a 100's sieve. In a sample unlikely to contain magnetic material, the adventitious iron from the crusher may be removed by a magnet. About 10 g. of material should be prepared, re-dried if necessary, and consigned to a stoppered weighing bottle. The pycnometer (weighing bottle type) must be of glass and of good quality, provided with a capillary in the stopper and with the mouth of the vessel ground flat so that no recess exists when the stopper is in place. An accurate chemical balance should be used and weighing carried to the third decimal place in grams. The atmosphere should be at $20° \pm 1°$. The bottle and stopper are thoroughly cleaned, dried at 110°, cooled and weighed; let the weight be p. After complete filling with distilled water at the above temperature, the bottle is reweighed (w_1). Now re-dry at 110° and put in about 2 g. of the sample and weigh the bottle, powder and stopper; let the weight be w. Now fill about one-third full with distilled water, re-inserting the stopper with a small piece of paper to prevent sticking and boil carefully for about fifteen minutes. (An alternative method is to warm slightly and place in a vacuum desiccator for a time, depending on the nature of the sample.) Fill to the base of the neck with pure water and allow to cool to the standard temperature (see above). When cooled completely and the sample settled, fill up, insert the stopper carefully and wipe dry with a soft cloth, with a minimum of handling; weigh (w_2). It can be shown, if the true specific gravity is G_t, and no change in total volume occurs on mixing water with the sample, that

$$G_t = \frac{(w-p)}{(w-p)-(w_2-w_1)}.$$

Two determinations should be averaged and should check one another to within 0·005.

The three vital points, requiring particular attention where great accuracy is required, are removal of air, correct temperature when exactly filled and density of the liquid. The pycnometer may be used at any desired temperature, if calibrated with water at that temperature, using a standard table of densities of water. If paraffin is to be used, the calibration with paraffin must follow that with pure water, observing the strictest cleanliness. The data give the true volume of the pycnometer and the density of the paraffin oil at the desired temperature. To correct for density of the liquid in the

[1] *J. Amer. Ceram. Soc.*, 1928, 11, 475; *ibid.*, p. 453.

above formula multiply the numerator ($w-p$) by d, the density of the water or paraffin used. Densities should be followed by an indication of the temperatures involved, thus 1·56 (20°/4°) indicates a density of 1·56 determined at 20°, but compared with water at the standard temperature of 4° (the temperature of maximum specific gravity). Corrections for air-displacement may be made on reference to standard tables.

The Grading of Clays according to Size of Grain

1. **Sieving.**—The clay technologist takes a special interest in material which is too fine to be separated on existing standard sieves or lawns. An intimate knowledge of the particle-sizes of the finest material is usually not obtained in an ordinary technical examination; consequently, apart from the intrinsic usefulness of a knowledge of the quantity and size-distribution of the *coarser* matter, its characteristics are often a useful guide as to what to expect in the sub-microscopic portion. Furthermore, the ceramist deals largely with finely ground minerals, chief amongst which are flint (pre-calcined) and quartz, felspar, Cornish stone (a raw material primarily useful for its felspathic content), calcined bone-ash, and various synthetic glassy materials used as glazes. In such materials the average fineness or, alternatively, the surface factor is such that the information obtained by combining the results of sieving and elutriation or sedimentation tests (see p. 45) is often sufficiently exhaustive for practical purposes.

Sieving may be carried out wet or dry; but where any large proportion of fine material is present the wet process is preferable. The residues on the sieves should be washed perfectly clean, and this operation aided by rubbing to a degree which does not cause appreciable grinding of the particles or damage to the sieve. The aim of ordinary analysis of particle-size is to obtain the size-distribution of the primary particles, and, particularly with clays, the utmost care must be taken to ensure that secondary aggregates are broken down and that reflocculation does not occur during the examination of the portion which passes through the sieves. The standard sieve-sizes of the Institute of Mining and Metallurgy (I.M.M.) are suitable, and particulars of these are given in the table on p. 38.

As J. W. Mellor[1] states, "Ordinary lawns of an equivalent size will probably suffice for works practice, and it is possible that in particular cases a set of three other sizes might be more convenient. All depends on the standard coarseness of the material employed in the works." All, or most of the above sizes may be used to advantage in defining the grading of silica brick mixtures. For elutriation tests on ceramic materials, the successive residues on the 120's and 200's lawns are

[1] J. W. Mellor, *Trans. Ceram. Soc.*, 1919, 18, 251.

taken, as a preliminary to the hydraulic separation. The residues are carefully washed on the sieves, dried at 110° and weighed. (*Note:* Potters usually reject residues on a 120's lawn.) It should also be noticed that the meaning of a sieve analysis depends, to some extent, on the prevailing shape of particle of the material examined. Both sieving and methods depending on the suspension of the particles in some such medium as water, depend chiefly on only two of the dimensions of the particle, and, whereas the material passing a sieve is governed largely by the minimum cross-section of the particle,

Standard Sieve Sizes of I.M.M.

Mesh, *i.e.* Apertures per linear inch.	Diameter of Wires.		Diameter of Aperture.		Screening Area, per cent. Holes.
	Inch.	Mm.	Inch.	Mm.	
5	0·100	2·540	0·100	2·540	25·00
8	0·0625	1·587	0·0625	1·587	24·60
10	0·050	1·270	0·050	1·270	25·00
12	0·0416	1·059	0·0416	1·059	24·92
16	0·0313	0·795	0·0312	0·792	24·92
20	0·025	0·635	0·025	0·635	25·00
30	0·0167	0·424	0·0166	0·421	24·80
40	0·0125	0·317	0·0125	0·317	25·00
50	0·0100	0·254	0·0100	0·254	25·00
60	0·0083	0·211	0·0083	0·211	25·00
70	0·0071	0·180	0·0071	0·180	25·00
80	0·0063	0·160	0·0062	0·157	24·60
90	0·0055	0·139	0·0055	0·139	24·50
100	0·0050	0·127	0·0050	0·127	25·00
120	0·0041	0·104	0·0042	0·107	25·40
140	0·0036	0·091	0·0036	0·091	25·00
150	0·0033	0·084	0·0033	0·084	24·50
160	0·0031	0·079	0·0031	0·079	25·00
170	0·0028	0·071	0·0028	0·071	25·00
200	0·0025	0·063	0·0025	0·063	25·00

the other separations depend to a similar extent on the maximum cross-section.

Fineness of Wet-Ground Enamel.[1] For ordinary control purposes it is required to know the residue between 40's and 200's sieves from 100 g. of the suspension in water. The following method is suggested.

The bulk material in slop form is stirred thoroughly and a 100 g. sample taken. A No. 40 sieve (opening 0·0166 in.) is placed on a No. 200 sieve (opening 0·0029 in.). The sample is poured on to the upper sieve and carefully washed through with water until the washings are free from enamel. Only coarse, unground particles should remain on the 40's sieve, which serves as a protection for the 200's. Dry the lower sieve with its contents until the residue easily moves about as a dry powder when shaken. Tap the sieve gently till no more powder

[1] *J. Amer. Ceram. Soc.*, 1928, **11**, 466; *Bull.*, 1927, **6**, 259.

passes through, transfer the residue to a balance and weigh to the nearest 0·1 g. The weight obtained is taken as an index of the coarseness of the enamel.

2. **Elutriation.**—The method of elutriation has been in practical use for many years in the pottery industry, chiefly for ground flint, but, to a less extent, for other ground materials and for clays. The method described by Mellor (*loc. cit.*, p. 37) is generally satisfactory, although it does not give an adequate indication of the fineness of most clays, as the greater part of the material is found in the finest fraction. The standard method is to make the following analysis, rejecting the coarsest residue.

Extreme Diameters, mm.	Average Diameter, mm.	Maximum Velocity, mm. per sec.	Surface Factor.
Below 0·01	0·0063	0·18 (overflow)	359
0·01 to 0·063	0·042	3·00 (in the elutriator)	53·9
0·063 to 0·107	0·087	- (on 200's lawn)	26·0
Above 0·107	–	– (on 120's lawn)	–

This procedure is very simple, as it involves but one separation in the elutriator, which can be arranged specifically for the one velocity; the test can be carried out overnight. Having obtained the percentages, on dry weight, of the various fractions, each one is multiplied by the corresponding surface factor, and the sum of the products is taken as a standard figure representative of the sample. The velocities are calculated from E. Schöne's formula for a specific gravity of 2·65.

The following data for quartz particles are given by A. Holmes.[1] The velocities corresponding to known diameters were experimentally determined: they were not found to agree well with calculations involving the usual restrictions.

Diameter, mm.	Upward velocity, mm. per sec. at 15° C.
0·40	47
0·30	32
0·25	25
0·20	20
0·10	6·7
0·05	1·8
0·01	0·12

The use of the higher velocities for separating coarser particles has the advantage that all the results are comparable, which is not the case when part of the data result from a sieve analysis.

[1] *Petrographic Methods and Calculations*, Part I., 1923, p. 207.

When a particle is allowed to fall in a liquid, its velocity at first increases, but, owing to the increasing resistance of the liquid to the accelerating particle, equilibrium is eventually established at some characteristic velocity. With spherical particles in a boundless liquid and in a certain moderate range of velocities, Sir G. C. Stokes calculated that the resistance to the passage of the particle was equal to 6π times the product of the viscosity of the medium, the radius of the particle and the velocity of the particle relative to the bulk of the liquid. This resistance is balanced by the effective weight of the particle, which can be expressed in terms of its radius and the difference between the densities of the particle and the liquid. Equating these two expressions for the resistance, we get the well-known Stokes's law,

$$r^2 = \frac{9}{2} \cdot \frac{\eta}{(\rho - \rho_1)g} \cdot v \quad . \quad . \quad . \quad . \quad (1)$$

where r, ρ, v are the radius, density and velocity, respectively, of the particle, η, ρ_1, are the viscosity and density of the medium, and g is the acceleration due to gravity.

This law includes the case of particles rising in a less dense medium, or of particles stationary in a current of liquid of a velocity just sufficient to counteract the tendency to sink or float. This relationship, and kindred ones, are used for the grading of particles, either by studying the state of affairs during settling in a still liquid (see later) or in an upward current in an elutriator. The latter is theoretically simple, as it allows of a direct division of the material into grades between certain limits of size. The two chief difficulties with normal materials are erratic currents and eddies, due in part to small temperature variations, and the impracticability of providing the theoretical requirement of a stream of liquid flowing upward with the same velocity at every part of a given horizontal plane. In all elutriators, a vessel tapering from above downwards is provided, with an upper surface or, better, cylindrical section, calculated to give a velocity, such that all particles of less size than a chosen value are carried over. Unfortunately, in a tubular or conical vessel the velocity of flow at the periphery is zero, and, at the axis, a maximum. Consequently, the surfaces of equal velocity are domed in shape. Three consequences of this are that (*a*) fine particles which should be washed over collect around the periphery and it is difficult to remove them all; (*b*) particles which have practically come to rest high up on the dome of equal velocity tend to roll down this surface and accumulate near the sides of the vessel; (*c*) the average velocity of flow is less than the maximum velocity, though a large proportion of the particles will be controlled by this maximum. The first two factors tend to lengthen the time required for elutriation and destroy the sharpness of the

separation. A method used for counteracting these troubles is to stop or slow down the flow of liquid periodically and siphon off the contents of the cylindrical portion of the elutriator, subsequently stirring up the residue and continuing the elutriation. The third factor is allowed for empirically. It will be seen that the ideal conditions of Stokes's law are not fulfilled in several respects. Further, in technical practice the shape and nature of the surface of the particles, and their specific gravity, are all liable to greater or less variation, even in a single sample. The actual relations obtained empirically by E. Schöne, with his elutriator, are given by the formulæ:—

$$D = 0.0518 \frac{V^{0.636}}{(S-1)} \qquad (2)$$

$$V = 104.7\,(S-1)^{1.57} D^{1.57} \qquad (3)$$

$$D = 0.0314\, V^{0.636}, \text{ where } S = 2.65 \qquad (4)$$

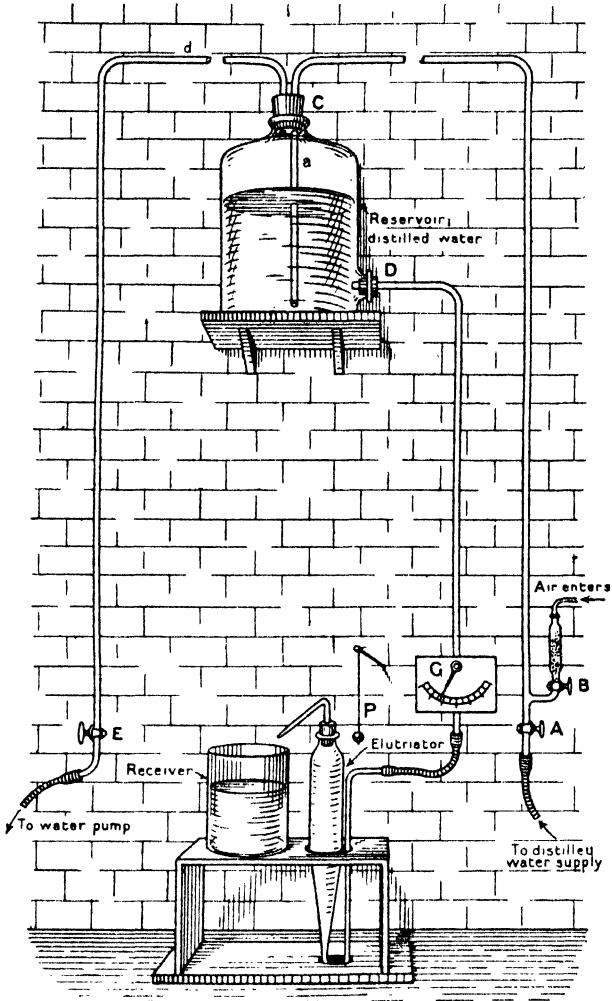
D = mean diameter of particle, mm. V = mean velocity, mm. per second.
S = specific gravity of suspended particles.

The formulæ apply for water as suspending medium and velocities between 0·1 and 12 mm. per sec. Formula (4) is normally used; formulæ (2) and (3) are required if the density differs seriously from 2·65, the density of quartz. Calculations may conveniently be carried out using logarithms. The formulæ are stated by J. W. Mellor (*loc. cit.*) to agree very closely with actual measurements.

The original apparatus of Schöne was provided with a constant level tank for the supply of water to the bottom of the elutriating vessel, and an overflow-tube fitted with a manometer and a small jet for the escape of the water. The modified apparatus of Mellor, arranged for the use of distilled water, is shown in Fig. 3 (p. 42). Tap-water, maintained at a constant level by a ball-cock, is permissible only where the water is exceptionally pure, or where control-tests are required for works' use on a material such as ground silica, which is not very susceptible to flocculation (clotting).

"A 20 litre aspirator bottle is fitted with a rubber stopper C, and two glass tubes. One tube, *a*, passes to the bottom of the bottle, and the opposite end dips into the laboratory stock of distilled water. A two-way stop-cock A is placed conveniently, and a side-tube is fitted with a stop-cock B and a cotton-wool filter to remove dust from the air which passes through. The other tube *d* passes to the filter-pump and has a stop-cock, E, fitted in a convenient place. The tubulure D is closed by a one-hole rubber stopper and fitted with a tube to lead water from the bottle to the elutriator. (The indicator stop-cock is not required unless a system of fractionation, other than that indicated below, is employed.) This tube is connected with the indicator stop-

cock, G, for regulating the velocity of the water flowing through the elutriator. To fill the reservoir bottle with distilled water, close the stop-cocks G and B; connect the tube *a* with the distilled water bottle; connect *d* with the filter-pump and distilled water will pass into the

Fig. 3.

reservoir. When the reservoir is full, close A, open B, and stop the connection with the filter-pump at E when the water has been cleared away from the tube *a*. When the stop-cock G is open, the water will run from the reservoir at a constant pressure since the reservoir acts as a Marriotte's bottle."

The elutriator stand also supports a large vessel under the nozzle whence the overflowing liquid falls, and this nozzle, in the absence of a manometer, may conveniently be restricted to about 1 mm. diameter and the speed of dropping corresponding to the required velocity be made equal to the time of swing of a small pendulum arrangement (P in Fig. 3) having a weight suspended by a string about 10 in. long. In case any trouble is experienced with clotting and collection in the bottom bend of the elutriator, a little mercury, or shot No. B or BB, to fill about 2 or 3 cm., may be introduced.

It is necessary, before use, to test the cylindrical part of the elutriator for uniformity. Fill the conical portion with water and mark the level with gummed paper. From a burette run in 20 c.c. of water, mark the new level and measure the rise. Continue the process with further 20 c.c. portions up to the top. If there are only deviations near the top and bottom of the cylindrical part, reject these and average the rest; otherwise, the elutriator itself must be rejected. Calculate the average cross-section by dividing the rise in level into the volume of the cylinder, giving, say, s sq. cms. = 100 s sq. mm. Then, with the apparatus assembled, if a velocity of v c.c. per sec. of outflow is obtained with a stream-velocity of V mm. per sec., we get the relationship:

$$0.1\, s\, V = v$$

or,

$$V = \frac{10}{s} \cdot v \text{ mm. per sec.} \qquad . \quad . \quad . \qquad (5)$$

Find v for a dozen positions of the indicator index of the stop-cock controlling the inflowing water and calculate V. Plotting V against the position of the indicator gives a graph from which the indicator may be set for any desired rate.

Other forms of apparatus are constructed in metal, such as brass or copper, for works' use. That of B. Moore[1] and the improved Schultze apparatus are largely used. A complete description of the latter is given by H. Harkort.[2] In this apparatus a concatination of separating vessels of successively increasing diameters divides the material into the desired fractions.

Preparation of the Sample. The usual aim is to find the grading of the ultimate particle-sizes and, consequently, it is necessary to break up all floccules and clots. At the same time, the treatment must not be so drastic as to reduce the sizes of the primary particles. With many ground materials, it is usually considered sufficient to weigh out 10 g. of material, place this in a bottle with distilled water and shake in a mechanical shaker for four hours. The contents are then transferred to a 120's sieve, placed over a 200's sieve, and the residues on the sieves carefully washed, dried at 110° and weighed. All the

[1] *Trans. Ceram. Soc.*, 1921, **20**, 112. [2] *Ber. deut. Keram. Ges.*, 1927, **8**, 6.

water and fine material passing through the finer sieve is put into the elutriator. The finer portions of ground flint usually contain a small percentage of lime. The author advises the solution of this by the addition of sufficient dilute hydrochloric acid, as the lime has a definite coagulating effect which is not so noticeable after the solution of the lime; the solution is, of course, rapidly removed in the ordinary course of the elutriation.

The difficulties of deflocculation in clays may not always be satisfactorily overcome, as certain coagula occur which are only broken by such severe treatment as will cause a partial solution of the clay. Some of the methods mentioned below are subject to this criticism; severe treatment may, however, be considered to be justified in some cases.

J. W. Mellor (*loc. cit.*) says that some clays may require weathering or washing free from soluble salts, or both, while certain bases such as lime may give rise to persistent flocculation. After the necessary preliminary treatment, 10 g. of the clay is shaken in a mechanical shaker for four hours (or more, as required) with distilled water containing 1 to 2 per cent. of ammonia or ammonium carbonate. The prepared material is passed through a 120's lawn, the residue being washed with distilled water, dried at 110° and weighed. The residue on the 200's lawn is similarly treated, and all the matter passing this lawn is transferred to the elutriator.

Schloesing's method[1] is to extract the clay with nitric or hydrochloric acid (a maximum concentration of acid of 0·5 per cent. is fairly satisfactory) and then wash until the filtrate is no longer acid. This removes soluble salts and most of the basic ions of the gels. Ammonia in proper proportion for deflocculation or separation of the clots is then added. H. E. Ashley[2] recommends a preliminary series of tube settling experiments, with 5 g. of clay in each of a series of stoppered graduated 100 c.c. cylinders. Caustic soda is added in progressively increasing amounts. The amount of alkali which will give a minimum volume of clean-grained sediment is chosen and this proportion, based on the weight of dry clay used, is taken in preparing a sample for elutriation. Fuller reference to the technique of this method is made later under Slip Casting. It may be noted that in the presence of coagulating bases of the alkaline earth group, and some others, caustic soda does not effect the necessary complete separation. There seems no valid objection, in ordinary elutriation, to the substitution of silicate of soda (which is much more widely effective) for caustic soda. The suspension thus obtained is protected by the silicic acid precipitated on the grains, whilst the

[1] *Comptes rend.*, 1903, **136**, 629; 1903, **137**, 369.

[2] "Control of the Colloidal Matter of Clays," Tech. Paper, Bureau of Standards, 1913.

increased size of particle is generally not appreciable within the range of particle-size retained in the elutriator. Alternatively, the method of Schloesing may be combined with Ashley's method.

As the greater part of many clays is carried over in the finest fraction, which involves a very considerable time and volume of water, and that water exerts a marked solvent effect on some of the minerals present, Ashley (*loc. cit.*) proposes a useful combination of elutriation with sedimentation. The greater part of the sol is removed by sedimentation and decantation four times repeated, using distilled water and removing 90 per cent. of the liquid each time; the granular residue may then be elutriated with tap-water. For instance, where 50 g. of clay was treated, and thirty minutes allowed for each sedimentation, it was found that 0·3 per cent. of crystalline matter which ought to have remained in the third can of a Schulze apparatus was lost, the average diameter of the particles being 0·167 mm.

Separation of Grades. In the method given by Mellor (*loc. cit.*), where only one separation is required, the pendulum is used to synchronise the rate of dripping of the effluent, which is continued until the water is quite free from suspended matter. The residue in the elutriator is then washed into a basin, dried and weighed. This, with the residues on the 120's and 200's lawns, gives the fine fraction by difference. For greater accuracy, the whole of the overflow from the elutriator may be made up to a definite volume, agitated and an aliquot part (*e.g.* 200 c.c.) taken and evaporated to dryness, and the residue weighed. Otherwise 200 c.c. may be taken at various depths and each dried, and the weights of residues averaged and multiplied by the ratio of the original volume to 200 c.c. The final results may be expressed as percentages and the surface factors of the fractions calculated and added together.

3. **Sedimentation.**—When a well-mixed suspension consisting of particles of uniform density is allowed to settle under the influence of gravity, the suspended matter accumulates in a manner which is characteristic of the size-grading of the suspension. Similar characteristics apply to the concentration, or the hydrostatic pressure of the remaining suspension at any level. The relations between the data obtained by these methods and the distribution of the particles in respect of size have been worked out principally by S. Odén.[1] Odén developed a method involving weighing the sediment; a suitable automatic balance, devised by S. Odén and B. A. Keen, is now on the market. Fig. 5 illustrates the construction. Sedimentation methods are advantageous in that they give a continuous distribution-curve; this is obviously much more informative than the discontinuous data of elutriation. Furthermore, the minimum size of grain which can

[1] *Colloid Chemistry*, ed. by J. Alexander, 1926, vol. i., p. 861.

conveniently be determined by settling is of the order of 0·5 μ, as against the 5 μ or 10 μ of ordinary elutriation. Also, various media of greater or less viscosity and density than water can be used so as to extend the range of the investigation, and this without the trouble and expense that would be involved in using special liquids in an elutriator. The following quotation from B. A. Keen[1] explains the use of Odén's accumulation-curve. "A flat pan attached to one arm of a delicate balance is immersed in the soil suspension, and the increasing weight, P, of particles settling on the plate is measured from time to time. The curve obtained by plotting these results is called the accumulation-curve (Fig. 4), and from it the distribution-curve can be derived graphically or arithmetically as follows. At the end of time t all particles whose radius r is greater than a certain value will have reached the plate. In addition there will still be falling on the plate, particles whose radius is less than r. The actual rate of increase of weight $\frac{dp}{dt}$ at time t is, therefore, due to this latter group alone, and since they have been falling at this constant rate from the beginning of the experiment, the actual weight of these smaller particles on the plate is simply $t \cdot \frac{dp}{dt}$. From the geometry of Fig. 4 this expression is given by the intercept cb. The total weight, P, at any time t being Oc, the weight of particles, S, in the suspension having a radius equal to or greater than r is given by Ob. The value of r is obtained from Stokes's relation, $r = \sqrt{\frac{x}{Ct}}$ where x is the depth of the pan below the surface of the liquid and C is a constant. By repeating this graphical process for different values of t, the weight of particles S between any desired values of the radius can be obtained by difference. The actual distribution-curve is obtained by plotting $\frac{dS}{dr}$ against r, and from it the percentage weight of particles between radii r_1 and r_2 is given by the ratio of the area under the curve between the perpendiculars drawn at r_1 and r_2 to the total area under the whole curve. This is equivalent to obtaining the integral $\int_{r_1}^{r_2}\frac{dS}{dr} \cdot dr$. The graphical method is, of course, unsuitable

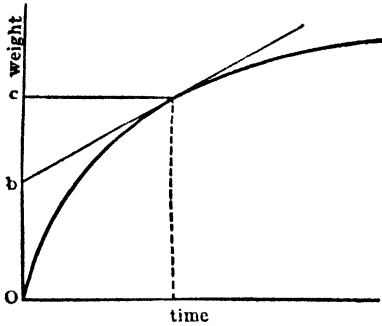



FIG. 4.

[1] "The Physics in Agriculture," art. in *Physics in Industry*, 1920.

for obtaining the values from which the distribution-curve is constructed. They are obtained arithmetically from the experimental values by the formula:

$$\frac{dS}{dr} = \frac{2t^2}{r} \cdot \frac{d^2P}{dt^2}.$$

For particles of a large range of sizes the distribution-curve can be made more compact by using $\log_e r$ instead of r, and $\frac{r.dS}{dr}$ instead of $\frac{dS}{dr}$. The curve assumes a somewhat different shape, but the area ratio under any portion of it is unaltered."

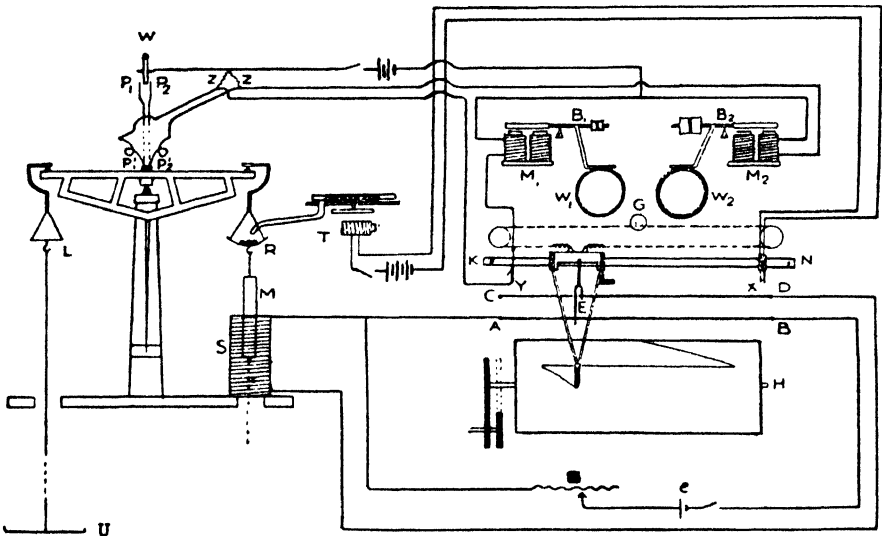



FIG. 5.

The complete mathematical treatment is given by Odén (*loc. cit.*). Fig. 5 shows diagrammatically the Odén-Keen balance. This "consists of a suspended plate, U, attached to one arm of a balance, which is kept in equilibrium by an automatic adjustment of the current by a solenoid, S, attracting a permanent magnet, M, suspended from the second arm of the balance. When the weight of the sediment reaches a given amount, *i.e.*, when the solenoid current reaches a given value, a small metal sphere is automatically placed on the second pan of the balance, R, and the solenoid current returns to a smaller value. The strength of the current is recorded on a moving paper band, H, and the operation just described results in a curve presenting a number of steps. A very open and sensitive scale can therefore be used for the curve, although the actual trace is confined within narrow limits

of width. The sensitiveness of the record can be modified or increased by suitable adjustments of the component parts of the instrument. The periodic replacement of the electro-magnetic attraction by the metal balls result in the sensitiveness in any given experiment remaining constant." This instrument, with water as suspending medium, may be used over the range 20 μ to 0·1 μ (0·02 mm. to 0·0001 mm.) and, as already mentioned, the range may be extended, particularly upwards, by changing the medium. The concentration of the suspended matter used is about 1 per cent., and this low value is a great aid in avoiding flocculation of the finer particles. Any of the methods previously discussed for the preparation of the sample may be used: Odén advocates the method of W. Beam.[1] The sample is rubbed gently with a stiff brush, adding ammonia solution up to

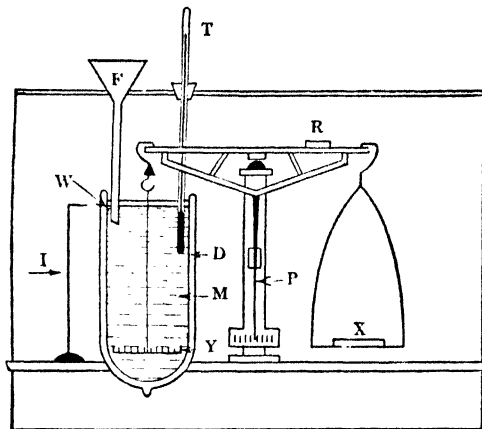



Fig. 6.

a concentration of 0·1 *N*, followed by shaking the suspension for twenty-fours hours without boiling.

The method of J. H. Calbeck and H. R. Harner, as adapted by H. N. Holmes,[2] serves a similar purpose to that of Odén and Keen, without the expensive complications of the latter. The apparatus is illustrated in Fig. 6. The following is a description of its use in the particle analysis of a pigment. "D is an unsilvered Dewar vacuum tube about 19 cm. long and 4 cm. inside diameter used for a settling chamber, the medium, M, is covered with a thin layer of water, W, to prevent evaporation. The pans, Y and X, are adjusted so that they balance exactly when D is filled with pure medium covered with a thin layer of water. The tube is then removed, emptied and cleaned and put back in position without disturbing the adjustment of the

[1] *Rep. Wellcome Trop. Res. Labs., Khartoum, Chem. Sect.*, 1911, pp. 34-45.

[2] *Laboratory Manual of Colloid Chemistry*, 2nd ed., 1928, p. 5.

balance. About 0·5 g. of pigment is thoroughly dispersed on a plate with a spatula and washed into a flask with a measured volume of medium and, after thoroughly shaking and adjusting to 25°, the suspension is poured into the tube rapidly through the funnel, K, and a measured volume of water poured on at once to form a seal. The suspension should come exactly to the level indicated by the pointer, I. A stop clock is started as soon as the water has been poured in. The suspended pigment begins settling out on pan Y. The balance arrest has been adjusted so that the beam can swing freely through a very small angle. The adjustment is now made so that the pointer can swing freely only one scale division right or left of the centre mark, allowing the pans a vertical movement of less than 2 mm. If a 5 mg. weight is placed on pan X prior to pouring in the suspension, the amount settled out by the time the suspension is poured in and the water-seal made will not have exceeded the 5 mg. and the pointer will be at the left of the centre point. However, it will begin to swing slowly to the right, and when it reaches the central division mark the time is noted and another 5 mg. weight placed on the pan. The pointer swings rapidly to the extreme left position, and when it again swings to the central point, the time is taken and another small weight added and so on until the sedimentation is complete." A concentration-curve is prepared from the data and treated as described above. The maximum size of particle settling at any time t minutes from the start in a column h cms. high above the pan Y may be calculated from Stokes's formula putting $v = \frac{h}{60t}$.

In applying Stokes's law it must be realised that the ideal conditions are not satisfied; the movement of the particles gives rise to an upward displacement of water, the settling of the suspension beneath the pan causes a slight current from the edges of the pan inwards, the shape of the particles is usually other than spherical, so that what is calculated is merely an *hydrodynamically equivalent* radius; variations in the specific gravity of the particles may occur; the mean specific gravity of aggregates accidentally occurring may be much less than is supposed; some of the particles may be so small that Stokes's law does not strictly apply. For this latter contingency, Cunningham's correction may be utilised; v, in the law, is multiplied by the factor $\left(1 + A\frac{L}{v}\right)$ where A is a constant depending on the material, and L is the mean free path of the molecules of the medium. A may be calculated from measured radii corresponding to known values of v.

G. W. Robinson [1] examined uniform suspensions after settling by

[1] *J. Agric. Sci.*, 1922, **12**, 306.

sampling with a pipette at a fixed depth (*cf.* p. 591). A. N. Puri and B. A. Keen[1] investigated the concentration of suspensions at increasing depths. G. Wiegner[2] and others measured the variation in hydrostatic pressure at a given depth in the suspension by means of a side-tube filled with medium. The distribution-curves can be derived from the data and the method is available, in the ordinary way, for the range 50 μ to 5 μ. Difficulties associated with slight temperature changes and the very small movement to be measured, were experienced. Improvements were made by Wo. Ostwald, v. Hahn and W. J. Kelly.[3] Kelly's tube, shown in Fig. 7, employs the

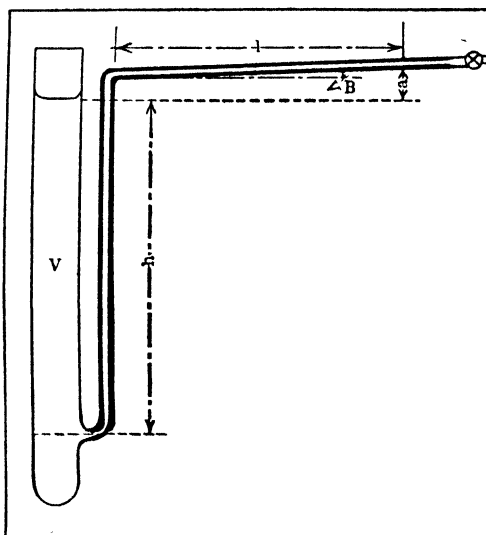



FIG. 7.

principle of an inclined tube, sometimes seen in delicate manometers. The bore of the manometer tube must necessarily be very fine as the bulk of moving liquid is magnified in proportion to the magnification of the reading, and the intrusion of the medium at the base of the settling tube is a source of error. The weight of the material which has settled past the end of the witness tube follows directly from the change of density given by the calibrated inclined tube; after obtaining the accumulation data in this way, their treatment is similar to that given for the sedimentation-balance. U. Pratolongo[4] and H. G. Schurecht[5] investigated the change in apparent weight of

[1] *J. Agric. Sci.*, 1925, **15**, 147.
[2] *Landw. Versuchsstationen*, 1918, **91**, 41.
[3] *Ind. and Eng. Chem.*, 1924, **16**, 928.
[4] *Staz. speriment. agr. Ital.*, 1917, **50**, 117.
[5] *J. Amer. Ceram. Soc.*, 1921, **4**, 812.

a plummet suspended in the upper part of the suspension, but did not attempt to derive distribution-curves.

Another method of attack is to place a layer of suspension at the top of a column of the medium, when the falling particles will separate directly into size-grades. F. F. Renwick and V. B. Sease[1] poured the suspension on to the top of a column of gelatin solution and, after a suitable time, caused the gelatin to set and prepared sections and

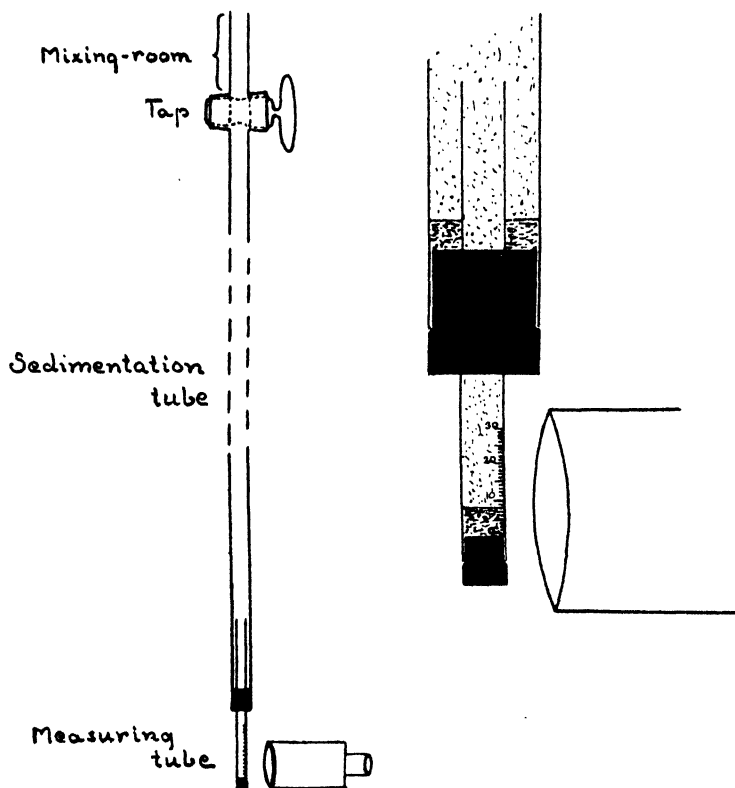



Fig. 8.

photomicrographs. D. Werner[2] devised a method, depending on the accumulation of the sediment, which has proved very valuable in the examination of soils, and, it would appear, might be equally useful in the study of ceramic materials. This is shown in Fig. 8. The volume (height) of sediment is measured periodically in a calibrated settling-tube. This is permissible for independent, similarly shaped and closely graded particles, as the volume of the sediment is practically proportional to its weight, independently of the size of grain. The apparatus has the

[1] *Phot. Jour.*, 1924, **64**, 360; *2nd Colloid Sympos. Monogr.*, 1925, p. 37.
[2] *Trans. Faraday Soc.*, 1925, **21** (2), 381.

advantage of simplicity. A short tube contains a concentrated suspension which is separated from the main column of clear medium, 1½ in. in length, by a tap of bore equal to that of the tubes. The abnormal conditions in the neighbourhood of the walls of the long tube are eliminated by a smaller tube inserted into the bottom end. This small tube is finely graduated to measure the height of the sediment.

The centrifuge has been used to assist gravity in the particle-analysis of material ranging from 1 μ down to 3 $m\mu$. For details and results of this method, reference should be made to The. Svedberg and H. Rinde,[1] and A. F. Josephs.[2]

4. **Direct Microscopical Measurement.**—Where a microscope with a micrometer mechanical stage is available, particles may be measured directly in two directions at right angles, the measurements being the difference of two micrometer readings with the screw travelling in the same direction. These two measurements are often taken as sufficiently representative, but the thickness, if required, may be measured with moderate accuracy with the help of a calibrated fine-adjustment screw. A mark on the glass slide immediately adjacent to the particle is first focussed sharply, the reading taken, and then, with the focussing screw moving in the same sense, the top of the particle is brought into focus and the reading again taken. The difference between the readings is the apparent depth; if the particle is immersed in a medium other than air, or the bottom mark is focussed through the particle, the distance measured should be multiplied by the refractive index to give the correct height of the particle. With the aid of a knowledge of the birefringence of the particle the thickness can be measured much more accurately (see A. Holmes, *loc. cit.*).

G. St. J. Perrott and S. P. Kinney[3] used the following method for work on pulverised fuel, measuring two dimensions and the number of particles in a preparation which could be classified in the following sizes:—60 μ, 50 μ, 40 μ, 30 μ, 20 μ, 10 μ, 5 μ, 2 μ. The results were compared with air elutriation and with sedimentation in water, giving the following average diameters 32 μ (air); 32·5 μ (water); 35 μ (direct count). The sample was mounted in Canada balsam, diluted with 20 per cent. of xylol. A few drops of this mixture were placed on a piece of window glass and a small amount of the pulverised coal sample mixed with it until the particles were evenly disseminated in the balsam. Two slides 50 × 75 mm. were used for mounting the sample. A drop of the mixture of Canada balsam and coal was placed on the clean slide. The coal in this mixture should weigh about 0·002 g. A second thin

[1] *J. Amer. Chem. Soc.*, 1923, **45**, 943; *ib.*, 1924, **46**, 2677; *Kolloid. Z.*, 1925, **36**, 53.
[2] *Trans. Ceram. Soc.*, 1928, **27**, 1.
[3] *J. Amer. Ceram. Soc.*, 1923, **6**, 417.

slide was placed on top of the drops, the slides pressed gently together and slid backwards and forwards until there was an even distribution of the coal and balsam. The mixture should cover a circular space about 2 in. in diameter. A magnification of about 200 diam. was usual and counting was done with a calibrated micrometer eyepiece divided symmetrically into squares and each square again divided into hundredth-squares. The whole field was worked over, one quarter at a time, each particle being marked on a record-sheet under the size to which it most nearly approached.

Surface Factor

The most important information to be derived from a particle analysis by any of the above methods, is often summarised in a surface factor, *i.e.*, a number which expresses the area developed in one average unit of volume of the material. This has been done with ground materials such as flint and felspar, and will, no doubt, be done with clays when sufficiently reliable and exhaustive data become commonly available. Direct methods of measuring surface factors have consequently been the subject of investigation; so far, no general method is available, but the following methods may be mentioned as useful in specific cases.

An interesting method applicable to quartz sands is that of G. Martin, E. A. Bowes, and J. W. Christelow.[1] The sand is previously treated with hydrochloric acid to remove iron and soluble matter, and dried thoroughly. From 1 to 0·5 g. of the prepared sand is treated with 150 c.c. (or 100 c.c.) of standardised pure hydrofluoric acid solution in a celluloid or bakelite container closed by a solid rubber bung. The container is shaken at 150 to 200 cycles per minute under water at 25°, usually for one hour. The contents are then transferred rapidly and quantitatively to 100 c.c. of ice-cold, distilled water, filtered through a specially prepared platinum Gooch crucible, washed, dried at 110°, heated over a small flame and strongly ignited in a muffle furnace, cooled and weighed. The rate of loss of weight is compared with that, under identical conditions, from a block of quartz of accurately known dimensions. The surface of 1 g. of the sand sample is taken as bearing the same ratio to that of 1 sq. cm. of quartz as the rate of loss of weight of the sand does to the rate of loss from 1 sq. cm. of the quartz block. The surface factor is expressed directly as sq. cms. per g. of sand. Full details of the apparatus and methods of standardisation are given in the original paper.

The method of W. A. Kochler[2] has proved useful for silica and silicon carbide, but gives erratic results with kaolin. The method is based on the assumption that the specific surface of a powder is

[1] *Trans. Ceram. Soc.*, 1926, **25**, 57. [2] *J. Amer. Ceram. Soc.*, 1926, **9**, 437.

proportional to the amount of thorium *B* adsorbed under standard conditions. Relative surfaces of several powders were determined by placing equal weights of them in equal volumes of a radioactive solution, giving time for equilibrium to become established, withdrawing an aliquot portion of clear supernatant liquid, evaporating this to dryness and determining the activity of the residue with an electroscope. The thorium *B* was dissolved either in distilled water or ethyl alcohol with, in some cases, the addition of a little concentrated ammonium hydroxide solution. It was necessary to carry out a series of measurements with each material, varying the proportion of powder present, thus giving an adsorption-isotherm approximating to the Freundlich curve. This method is akin to ordinary adsorption tests described below. The rational basis for surface factors is the surface developed by unit volume. In practice the *weights* of the fractions are usually obtained, and a standard density of 2·65 assumed; where there is serious departure from this density, the factor may be corrected by multiplying by the proper specific gravity divided by 2·65.

In summarising the results of elutriation, the problem is to derive a suitable surface factor for the fraction which lies between two given diameters. As the range of particle sizes in the fractions is usually a wide one, considerable differences arise according to the assumptions which are made. J. W. Mellor[1] assumes, for purposes of calculation, that, if the range is divided up into an indefinite number of equal increments of diameter, an equal number of particles will fall in each division. Summing up the total volume of such a set of particles (integrating the volumes between the limits of diameter) and dividing by the range of diameters gives a mean volume from which the mean particle-diameter of the group is derived. Dividing, for each group, *six* by the product of 2·65 (sp. gr.) and diameter gives a surface factor in terms of the adopted specific gravity. If much departure from this figure occurs (as with well-calcined flint) the factors should be adjusted in the manner mentioned above. The method of summing up the partial surfaces of the fractions is given under Elutriation, p. 39.

The assumption made by Mellor is arbitrary, though probably no more so than a number of others which might be made.[2] Although the results of surface-factor calculations based on elutriation are of great value for some purposes, notably the control of grinding of potter's flint, it cannot be recommended where an important fraction of the material is carried over in the elutriation (last fraction). Particularly with plastic clays, a surface-factor of scientific accuracy should be sought from the information contained in a complete distribution-curve. If this distribution-curve is not sufficiently complete, calculations should be based on the part which is known, with an

[1] *Trans. Ceram. Soc.*, 1910, **9**, 94. [2] Cf. *ibid.*, 1930, **29**, 251.

appended statement as to the proportion and upper size limit of the unknown, finest fraction. The term " mean diameter " in this connection, has no meaning except in relation to some definite summation, such as the total of the diameters, areas, etc., of the particles, divided by their number. For ceramic purposes the most generally used mean diameter is that derived from the surface factor, *i.e.*, six times the reciprocal of the product of specific gravity and surface factor.

Adsorption Tests.—Clays, in common with many other fine-grained substances, show a marked tendency to adsorb a wide variety of reagents. This has been taken as an indication of colloid content; it is dependent on the surface factor, the chemical nature of the adsorbing surface and the nature of the substances previously adsorbed by the surface or combined chemically in it. The amount of adsorbed material has usually been taken as proportional to the colloids present, without any proof that a given quantity of colloid from different sources had the same adsorption capacity. The proportion of colloids so estimated, was taken as a measure of the plasticity. It is doubtful whether this assumption is justifiable, except for comparative purposes within rather narrow limits.[1] The results of adsorption tests may, for the present, be taken as a useful basis of classification having an important bearing on the primary surface developed (*i.e.*, "colloidality") and the plasticity, without being a definite measure of either property. Such data may be used, under special circumstances, to measure the amount of colloidal matter present: a sample of the pure colloidal fraction from the same material must first be separated. Thus, C. J. Moore, W. H. Fry and H. E. Middleton[2] allowed a suitably prepared suspension of clay to settle for twenty-four hours and considered that the matter still in suspension after this time was fine enough to be all colloidal. This was then rapidly separated in a centrifuge using a force 17,500 times that of gravity, collected on a Pasteur-Chamberland filter, dialysed, washed and dried at 110°.

The adsorptions of ammonia vapour by the above reference sample, the original soil dried at 110°, and the same after heating to 1130°, were all determined under similar conditions. While still at 110°, the sample was transferred to a Schwartz U-tube and weighed. The tube was connected to drying-tubes, the tube immersed in boiling water and the whole apparatus thoroughly evacuated. Then, with the U-tube in a bath at 0°, dry ammonia gas was passed in until adsorption was complete at atmospheric pressure, the sample being finally allowed to stand for an hour in a stationary atmosphere of ammonia. The

[1] A figure for the proportion of colloidal matter is, of course, given directly by the distribution-curve, provided this is known to relate to the completely dispersed material. The method of G. J. Bouyoucos provides a rapid approximation to such a figure. (*Science*, 1926, 64, 362.)

[2] *Ind. Eng. Chem.*, 1921, 13, 527.

ammonia was then drawn off into absorption-tubes filled with a saturated solution of boric acid: finally, the release of the ammonia was aided by placing the U-tube in boiling water and sweeping out with a current of air. The ammonia in the borate solution was determined by titration with $N/10$ H_2SO_4, using methyl orange as indicator. The calculation of colloidal matter in the soil was carried out by subtracting the small adsorption-value of the calcined soil from that of the raw soil and expressing the difference as a percentage of the adsorption shown by the fine fraction. The same three samples treated with malachite green, as described below (modified), gave the same result.

Ashley's Malachite Green Test is as follows:—20 g. of clay and 1·2 g. of dye are mixed with 400 c.c. of water in a 500 c.c. bottle with a ground-glass stopper greased with vaseline. The bottle is closed and rotated, end over end, at 60 r.p.m. for one hour, in the frame of a small ball mill. The suspension is then allowed to settle overnight; a portion of the clear liquid is placed in a comparison-tube, as used for steel analysis (carbon) and compared with a standard solution (3 g. per litre) of the dye, diluting the standard and using a camera for the matching. The remaining concentration of dye is expressed in g. per litre and the equivalent adsorption due to 50 g. of clay obtained by difference from 3 g. The results for different clays may be expressed relatively by taking a series of concentrations of a standard clay, say 5, 10, 20, 30, 40, and 50 g. per litre with 3 g. of dye in each case and plotting graphically the adsorptions against the amount of the standard clay present. Other clays are represented by a point on the graph corresponding to a given weight of clay. Doubling this weight gives a figure for adsorption relative to 100 for the standard clay. Where a fraction has been separated which is considered to be wholly colloidal, this is utilised as a basis of comparison and a standard adsorption curve is determined for the pure colloid and the adsorption value of the original clay is located on this curve and the result expressed as a percentage of colloidal material present. This method eliminates some of the most serious assumptions involved in expressing adsorption values as a measure of colloid content. A further error may, however, be caused by the non-colloidal matter having an appreciable adsorption value. In the modification to which reference was made in the last paragraph a preliminary treatment with $N/10$ solution of sodium oxalate, in slight excess over the calcium present, was followed by fifteen minutes' shaking; a 0·2 per cent. solution of malachite green was then added, the remainder of the process being as already indicated. S. Kondo[1] recommends the use of methyl violet *2B* in place of

[1] *J. Soc. Chem. Ind., Japan*, 1924, p. 1315.

the green dye. He also obtained satisfactory results with manganous sulphate.

The sodium carbonate adsorption method has sometimes been used in the attempt to get a figure representative of plasticity. One g. of the clay is allowed to reach equilibrium with a normal solution of sodium carbonate and the amount adsorbed deduced from a titration of an aliquot part of the supernatant liquid. The method is open to the objection that the excess of alkali is liable to have a solvent action.

Several useful additional tests have lately been developed, particularly in connection with the allied problems presented by soils. The chief of these are the methods for determining imbibitional water, heat of wetting and acidity (hydrogen-ion concentration or *p*H-value). These tests are rather of interest, at present, to the research worker than to the technical man. E. A. Fisher's[1] method for imbibitional water is to centrifuge a sample of the wet clay under a force 1000 times that of gravity for forty minutes and determine the volume of water retained per unit true volume of clay. From this is subtracted the volume of xylene retained by the same clay, dry, under the same conditions. The electrometric method for hydrogen-ion concentration is given by D. W. Randolph and A. L. Donnenwirth[2]; the colorimetric method, with a suitable range of dyes, is described by W. A Taylor.[3] Heat of wetting may be determined in an ice-calorimeter under proper conditions.

Viscosity of Suspensions or Slips, and of Clay Pastes

Viscosity is, in a general sense, the resistance which a fluid offers to flowing; for a general discussion see *Viscosity*, E. Hatschek, 1928. The definition and unit of viscosity are derived as follows. If a liquid covers a fixed plane surface of indefinitely large extent to a depth of 1 cm. and is there limited by a parallel plane of equal extent, and this plane moves at a velocity of 1 cm. per second in its own plane, the force, per sq. cm. of this plane, necessary to maintain its steady motion is numerically equal to the viscosity of the liquid. It is a measure of the internal friction which is uniformly distributed throughout the liquid. It is further required that the liquid shall flow smoothly, that is, that the conditions shall be such that no turbulence is present, so that the velocity gradient along a line joining the two planes is constant. The dimensions of viscosity are $[M]\,[L]^{-1}\,[T]^{-1}$. The unit of viscosity is commonly known as the "poise," a term chosen by E. C. Bingham in honour of Poiseuille; the viscosity of water at 20° is 1·005 centipoise. Fluidity is defined as the reciprocal of viscosity. The chief methods of measuring viscosity depend on (*a*) the flow of

[1] *J. Agric. Sci.*, 14, 204. [2] *J. Amer. Ceram. Soc.*, 1926, 9, 541.
[3] *J. Amer. Ceram. Soc.*, 1927, 10, 243.

the liquid through a tube; (*b*) the resistance to relative movement of two concentric cylinders, the space between which is filled with the liquid; (*c*) the time taken by a ball to fall out of a spherical cup, the space between ball and cup being initially filled with the liquid; (*d*) the time of fall of a sphere in a column of the liquid; (*e*) similar conditions to (*b*) but using two parallel discs; (*f*) the rate at which the vibration of a body, usually a horizontal disc suspended in the fluid by a torsion-wire, decays. The first of these methods is most commonly used. For purely comparative purposes, the tube may be replaced partially or completely by an orifice. Instruments of this type are entirely restricted to technical purposes where absolute values are not required. The varying degrees of turbulence introduced and the density of the suspension are usually ignored; consequently the values obtained are not even approximately proportional to the true viscosities; the method is, however, serviceable for many purposes, and has the merit of extreme simplicity.

The apparatus used for clays by J. W. Mellor, S. A. Green and T. Baugh[1] consisted of a glass cylinder of about 2 in. diameter, open at each end, supported in a vertical position and fitted with a rubber bung at each end. Through the upper bung, eccentrically, a glass tube projects into the cylinder to a short distance from the top of the lower bung. The lower bung has a short tube passing through it centrally and restricted at its lower end to an orifice of 2 to 3 mm. The vessel is filled to a convenient level and the upper bung and tube replaced while the thumb or a cap prevents flow from the nozzle. On releasing, the flow takes place at a steady rate, independent of the quantity of liquid present, after the principle of Marriott's bottle. As soon as the bubbling from the upper tube has become steady the time of flow of a measured 200 c.c. is taken with a stop-watch Three or more tests should be done in parallel and the results averaged. The apparatus is calibrated by taking the average time of flow with water. Dividing the flow-time of the slip by that of water gives the required relative figure. Wide variations of temperature must be avoided. The bubbling from the upper tube serves the additional purpose of keeping coarser particles in suspension in somewhat dilute or unusually coarse mixtures. Generally, however, the tests should be restricted to samples of such high viscosity that appreciable settling does not take place during the test. This covers most slips of commercial importance for body-mixing, slip-casting and glazing. Where concordant results are required, instruments should be duplicated accurately, but the normal use of the instrument merely calls for the maintenance of a given viscosity. The apparatus may be simplified by omitting the upper stopper and tube and filling

[1] *Trans. Ceram. Soc.*, 1907, 6, 54.

to above a fixed level on the vessel, rejecting the liquid flowing until the mark is reached, and then timing the flow of a convenient volume. Similar instruments may be constructed in metal for use on the works, with appropriate minor modifications.

A. V. Bleininger and M. R. Hornung[1] devised such an instrument in a convenient form: it is shown in detail in Fig. 9 and assembled for use in Fig. 10. The outlet is in the bottom cap, which is about $\frac{5}{32}$ in. thick and is perforated with a hole tapering from $\frac{5}{16}$ in. internally and above to $\frac{5}{32}$ in. below and externally. A rubber gasket is placed

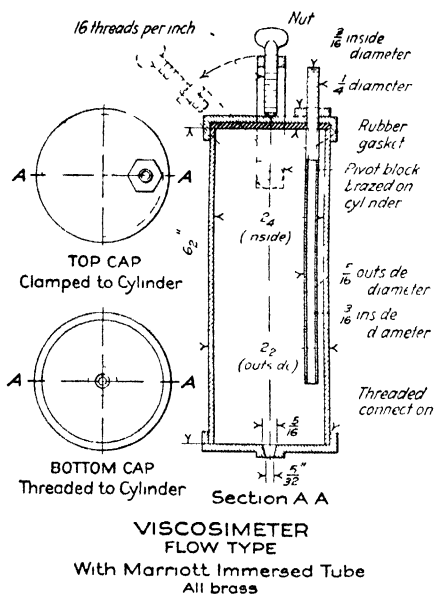



FIG. 9

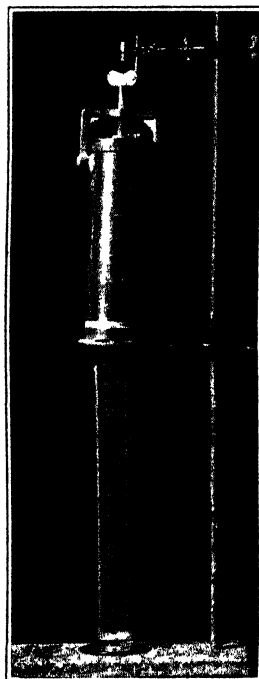



FIG. 10

under the rim of the cap and it is held in position by a stirrup having a central screwed rod and thumb-screw.

Fairly accurate measurements of the true viscosities of slips within a wide range of concentrations are possible with instruments designed in accordance with the principles of accurate viscosimetry (see E. C. Bingham[2]); special care should be taken that the velocities in the flow-tube do not exceed the critical velocities at which persistent turbulence is to be expected; further, the diameters of the tubes must be considerably larger than the coarsest particles present

[1] *Trans. Amer. Ceram. Soc.*, 1915, 17, 331.
[2] *Fluidity and Plasticity*, New York, 1922.

(whether primary or aggregated). It should be borne in mind that clay slips are normally highly coagulated and that such slips tend to assume a stable degree of coagulation which decreases with increasing steady shear of the slip. Where this feature is obtrusive it becomes difficult or impossible to co-ordinate results obtained with flow-tubes of different diameters, covering a wide range of viscosities, and an instrument of the concentric cylinder (Couette) type is then recommended. Where data on the variation of viscosity with concentration are required, it is essential to proceed by progressive dilution of a suspension of the highest concentration of the series: attempts to incorporate fresh dry material into the dilute suspension are usually highly unsatisfactory.

E. C. Bingham[1] has devised an accurate instrument for the study of the viscosity of concentrated suspensions (including clay slips) and masses of plastic consistency, which he has called a plastometer. The instrument is, essentially, a tube-viscometer having a brass body in three parts and a vertical glass capillary tube soldered into the basal plate of the body. A number of alternative capillaries of different characteristics are prepared, ready mounted in spare plates. The depth of material under test is ascertained by direct measurement through a glass window in the side of the instrument or by the insertion of a fine rigid wire and measurement of the soiled portion; to this must be added the length of the capillary and the average projection of the column of the material. Speedier flow of highly viscous materials is assured by the application of high pressures controlled by a column of mercury, needle-valves, a pressure-gauge, etc. Full details will be found in the original work to which reference has been made. The measurement of the amount of extruded material is a source of difficulty, the method adopted varying somewhat with the nature of the material under examination. The most direct method is to weigh the quantity extruded after the application of pressure for a given time, calculating the volume from the ascertained density of the material.

The interpretation of viscosity data of clay-water and similar mixtures is still a matter on which sharp differences of opinion exist amongst experts. Bingham's interpretation of viscosity concentration data is based on the assumption that the allied fluidity concentration curves are fundamentally linear. An interpretation based on the exponential relationship of S. Arrhenius, with due allowance for the sequestration of a portion of the medium in the interstices of aggregates present, gives, in the author's opinion, a more rational and general interpretation. Bingham's interpretation of the "plastometer" data is based on the assumption of perfect fluidity under pressure in excess

[1] *Loc. cit.*; E. C. Bingham and H. Green, *Proc. Amer. Soc. Test. Mats.*, 1919, [II], 19, 640.

of a certain critical value. While this is in accord with a certain theoretical conception of plasticity, it must be borne in mind that only some arbitrarily chosen conditions of experiment yield the required data, and that in no case does a progressive decrease of applied force actually give the expected critical value. An alternative interpretation is being sought in terms of the mechanical deflocculation to which reference has already been made, and this, in its turn, would be subject to the solution implied in Arrhenius's formula. Nevertheless, the viscosity data derived from the use of the "plastometer" are of the utmost value in that they give precise information of the greatest value for the empirical control of the consistency of a wide variety of "thick" liquids and pastes. Probably the most valued use of the method, up to the present, has been in the practical control of ready-mixed paints.

II.—EXAMINATION OF PREPARED MASSES IN THE PLASTIC AND DRY STATES

Plasticity

Plasticity, the most important property of clays in the raw state, and one with which every clay-worker is familiar, has so far eluded every attempt at precise definition to cover all that is implied in the ceramic meaning of the word. It is even doubtful whether this will ever be possible as some of the implications are contradictory. The essentials are, perhaps, implied in the term workability, meaning the power to be permanently distorted under a small force to a considerable extent without cracking. Generally, plasticity may be said to decrease with increasing tendency to crack on slight distortion, with increasing elasticity, with increasing additions of non-plastic matter, with increasing force necessary for deformation. On the other hand, the last factor is found to be so intimately bound up with the majority of the characteristics of plastic clays that it has been taken as a partial or total measure of plasticity. Plasticity, in general, is considered to increase with increase in the amount of water required for tempering, the range of water content at which the mass is workable, drying shrinkage, ultimate tensile strength in the plastic and dry states, ability to hold together non-plastic matter such as sand, ability of the dry clay to resist disintegration when placed in water, viscosity at a given concentration, water content of a suspension of a given viscosity, power of absorption of various substances, heat of wetting, degree of coagulation, imbibitional water, hygroscopic water, surface factor and closeness of packing of the particles. Only direct methods of estimating plasticity will be considered here, as reference is made to most of the other measurements elsewhere.

At present the only generally accepted test is the relative and qualitative test of the potter's thumb. By working a small piece of clay in his hands, pressing, rolling, bending and squeezing and noting the behaviour of the clay, the experienced clay worker is able to judge of its plasticity with fair precision. Different workers agree fairly well in the order of relative plasticity of a given series of clays. The method, is, however, too crude for many purposes; and some other, more readily measurable property, such as ability to hold non-plastics after drying, dry strength, moisture-content at the best hand-working state, etc., is then used.

Certain more direct tests have been developed, though not extensively used for technical examination. A. Brongniart[1] used a common wad-box, *i.e.*, a vertical cylinder from which the plastic clay was extruded in a solid cylinder of less diameter. He measured the length of extruded clay which would hang from the cylinder without breaking away and took the average of ten tests. The initial consistency, as governed by the proportion of water used in making the plastic clay, was judged by hand-working to be that of maximum plasticity. A sample was also dried out and the moisture-content noted. This method has been elaborated by B. Zschokke,[2] M. Rosenow,[3] and W. H. Artz.[4] Zschokke extruded a solid cylinder of prepared clay of 2·52 cms. diameter through two long collars of the diameter of the column. Smooth-bore collars were found to be satisfactory; blocks of larger diameter, moulded on the outer ends, were recommended for future work. Having filled both collars up close to the extruding die, the outer one was allowed to be pushed forward by the clay until a column of the desired length (5 cms.) was formed between the collars. The pair of collars, and the test piece held between them, was then severed and placed in a machine arranged to indicate the amount of extension produced on stretching to the point of rupture. A load was gradually applied and the machine arranged so as to give a diagram showing both load and extension in the form of a hump-shaped graph. The graphs and also the appearance of the broken test-piece were characteristic of the behaviour of the clay. Suddenly applied loads were found to give a much greater extension before rupture occurred. Normally the test was carried out with a slowly-applied load. A figure for plasticity was derived by multiplying the extension by the maximum tensile strength under standard conditions. This is equivalent to a measure of the work absorbed by the clay, chiefly in the neighbourhood of the "neck" where rupture

[1] *Traité des Arts Céramiques*, 1844, I, 252.
[2] "Argiles et la Ceramique," *Mém. Soc. d'Encour.*, 1906, p. 235.
[3] *Uber die Bildsamkeit der Tone*, Hannover, 1911.
[4] *Trans. Amer. Ceram. Soc.*, 1909, II, 411.

occurs. M. Rosenow (*loc. cit.*) used a similar method with a less intricate apparatus which merely indicated the amount of extension at the moment of rupture: the critical load was chosen by preliminary loading. In addition to the maximum load and extension, Rosenow considered that the moisture content of the plastic clay should also be included in the figure for plasticity. He, consequently, multiplied the three values together. This investigator carefully studied the effect of moisture content on the tensile properties for a variety of typical clays and found that the strength decreased and the extension increased with increasing moisture content, whilst the product of the former two factors tended to show a maximum at a certain moisture content. Nevertheless, Rosenow averaged the products, including moisture content, in arriving at his plasticity figure. It may be suggested here that the total moisture content is not so directly related to plasticity as is shrinkage-water; the proportion of this might, with advantage, be substituted for the total water present in such a figure as Rosenow's.

T. W. Talwalkar and C. W. Parmelee[1] examined cylinders of clay under torsion and obtained diagrams similar to the tension-figures of Zschokke. They concluded that a suitable index of plasticity was given by the ratio of total deformation at fracture in shear to the average stress beyond the stress-strain proportionality limit.

F. F. Grout's[2] test resembles essentially that of Zschokke in that the product of resistance to deformation and deformability is taken as a measure of plasticity. Grout deformed a cylinder of clay by loading it until cracks just appeared and measured the increase in area; the resistance was measured in terms of the load required to sink a Vicat needle to a definite depth in the clay. The method of G. Stringer and W. Emery,[3] described by J. W. Mellor, is essentially similar, but they use a small sphere of clay and measure the critical load and increase in area when cracking occurs. Other workers have used tests comparable with those already described; references are given by J. W. Mellor.[4]

W. E. Emley[5] designed a "plasticimeter," for plasterer's lime (*cf.* p. 316), which imitated the action of a trowel forced over the plaster at an angle of 10°, and measured the horizontal forces involved. The instrument has been used for examining clays and, in particular, the suitability of ceramic bodies for jiggering. For this purpose, F. A. Kirkpatrick and W. B. Orange[6] modified the instrument. They used a test-piece of 3·15 in. diameter and 0·25 in. thick moulded on

[1] *J. Amer. Ceram. Soc.*, 1927, **10**, 670; D. R. Irving and W. F. Dietrich, *ibid.*, 1929, **12**, 14; C. W. Parmelee and R. D. Rudd, *ibid.*, 1929, **12**, 552.

[2] *Geol. Sur., West Virgina*, 1906, **3**, 40; *J. Amer. Chem. Soc.*, 1905, **27**, 1037; *Trans. Amer. Ceram. Soc.*, 1912, **14**, 71.

[3] *Trans. Ceram. Soc.*, 1922, **21**, 93.

[4] *Comprehensive Treatise on Inorg. and Theor. Chem.*, 1925, **6**, 485.

[5] *Trans. Amer. Ceram. Soc.*, 1917, **19**, 523.

[6] *J. Amer. Ceram. Soc.*, 1918, **1**, 170.

to a plaster disc of known absorption and mounted on a spindle rotated so as to rise slowly and regularly by the rotation of a threaded part of the shaft in a fixed nut. The specimen, in rising, pressed against a flat metal disc, the tangential drag (friction) on which was counterbalanced by a gravity balance. The tangential force was measured at frequent short intervals up to five minutes: it invariably increased in amount, on account of the plaster removing water progressively from the test-piece. The average tangential force was taken as an inverse measure of the working qualities under a jigger. The effect of the instrument is to measure the ability to spread out, without concern for the limit of deformation at which splitting at the edge may occur. Marked distinction was shown in the force-time curves between clays of known high and low plasticity, and between an un-aged porcelain body and the same aged for eight months. The normal method of preparation of the clay was to mix carefully to jiggering consistency, followed by maturing for sixteen to eighteen hours in a moist atmosphere.

Air in Plastic Bodies

Faulty mixing machinery, particularly pug-mills, may cause serious losses of ware due to warping, lamination and reduced workability resultant on poor elimination of air in tempering the clay, or even by working air into the plastic mass. A means of measuring the air thus occluded is therefore of value in tracing faults and modifying the mixing machines. H. Spurrier[1] describes a convenient apparatus, shown in Fig. 11. Samples of the plastic clay are boiled in a large iron pan under a funnel which collects the gases given off and directs them into a glass tube of 30 mm. diameter, which is drawn out at both ends, being connected at the upper end to an Orsat gas-analysis apparatus by means of a length of rubber tube controlled by a pinch-cock. The apparatus being assembled, the water is first of all boiled freely, allowing steam to sweep out the collecting apparatus for fifteen minutes. The pinch-cock is then closed, and weighed samples of prepared clay are inserted under the funnel and the water boiled very gently to disengage the occluded air. A sufficient quantity of clay is treated in this way to give a conveniently measurable volume of gas, which is then passed into the measuring tube and its volume measured. The temperature of the measuring tube should be taken. The gases may subsequently be analysed if desired.

The Slaking Test, a Measure of Binding-power

This test was originally devised by Sokoloff as a means of measuring plasticity. The clay in the form of a Seger cone is

[1] *J. Amer. Ceram. Soc.*, 1918, 1, 584.

thoroughly dried and then gripped upright in a wire framework and so placed in a wide glass cylinder that the test-piece is supported away from the bottom of the vessel. On filling up with water or admitting a very gentle stream from below, the piece will begin to take up water and fall to pieces. The time required for the clay to fall completely from its supports is taken. Highly plastic clays usually take longest, and clays or mixtures of low plasticity, the least time to disintegrate. A series of mixtures with a standard sand may be made

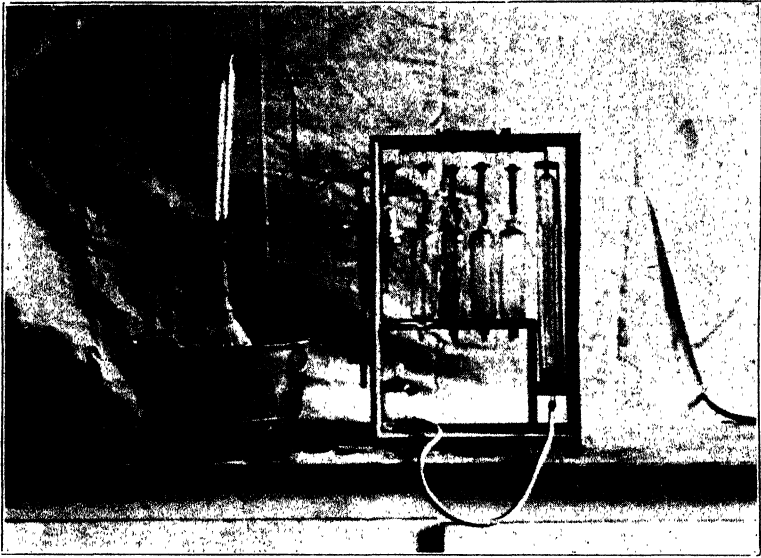



FIG. 11.

and the percentage of sand plotted against the time of slaking. The resulting curve indicates the ability of the clay to bond non-plastic additions.

The test has been standardised by the American Ceramic Society.[1] According to their specification, equal quantities of ground flint and the clay under test, ground to pass a 30's standard sieve, are mixed by hand or pugged to the best plastic consistency, batted out to a cake 1 in. thick which is subsequently subdivided into 1 in. cubes. The flint used is commmercial potter's flint, all passing a 100's sieve. The cubes are dried at room temperatures until air-dry, at 64° to 76° for at least five hours, immediately followed by drying at 110°, until approximately constant in weight. The pieces are cooled in a desiccator. A test-piece is placed on a $2\frac{1}{2}$ standard sieve.and immersed into water, at 25° ± 1° C. (77° F. ± 2° F.), without agitation of the water.

[1] *J. Amer. Ceram. Soc.*, 1928, **11**, 448.

The water must be at least 1 in. deep below the screen, and ½ in. to 1 in. deep above the top of the piece. The time in minutes is taken for the test-piece to slake and settle through the screen. The average of two separate determinations is required.

Binding Power for Sand

Bischof used this test for determining the quantity of any required non-plastic addition which could satisfactorily be held together by a given clay. For comparing clays, a standard sand, such as crushed quartz, passing a 20's and retained by a 30's sieve may conveniently be used. The clay, dried, crushed and passed through a 20's sieve is mixed with the sand in all proportions by 10 or 20 per cent. intervals, made up with the same proportion of water in all cases, rolled into small balls and allowed to dry. These are then tested for coherence, either by rubbing with a "camel-hair" brush or between the fingers. In this way, the mixture which just holds together is detected and the binding-power of the clay given as the percentage of sand held, based on the weight of clay.

Water Content

Hygroscopic Water. G. Keppler[1] determines hygroscopic water by keeping samples over 10 per cent. sulphuric acid in closed vessels until no further change in weight occurs. The weight of water retained, as determined by subsequent drying at 110,° expressed as a percentage on the dry basis, is the required figure. The method may be extended to give a series of data showing the amount of water adsorbed in equilibrium with air at various relative humidities and temperatures.

Tempering Water. The clay is mixed carefully to the consistency measured in any specified manner, or judged to be that of maximum plasticity, and a sample is weighed and dried to constant weight at 110°. The tempering water is expressed as a percentage of the dry weight. The average of three or more samples should be taken.

A convenient method, where many tests are required, and having a similar though less precise basis, is to use a metal or glass ring with end-plates enclosing a volume of 70 c.c. This space is filled with the clay in its plastic state, struck off level with a spatula and smoothed, turned over and the bottom similarly treated, and finally weighed. The ring and plate may be slightly oiled. If the weight is 120 g. or less the proportion of tempering water is high, indicating a "fat" clay, if 120 to 135 g. it is moderate, and if the weight is 135 to 140 g. the clay is "lean" or deficient in plasticity. The presence of calcium carbonate is a serious disturbing factor.

[1] *Ber. der Technisch-wissenschaftlichen abteilung des Verbandes keram. Gerwerke in Deutschland*, 1913, p. 18.

Shrinkage and Pore Water. The sum of these two is the tempering water, the pore water being that remaining when the main contraction of the piece ceases. Although in some clay mixtures shrinkage and the development of air-filled pores may be going on together during the greater part of the drying, a definite figure for shrinkage-water which is still of some significance may be obtained by dividing the volume contraction (c.c.) by the dry weight (gms.) of the test-piece and expressing the result as a percentage. The pore water then follows by difference from the total tempering water. In some cases the loss of pore water is accompanied by an appreciable bulk expansion of the clay.

Range of Workability

Any two sufficiently definite limits of condition of the clay-water system give a range of which the magnitude, in general, increases with the workability of the clay. The following is the method developed by A. Atterberg and examined by C. S. Kinnison.[1] About 5 g. of the clay powder of approximately 120 mesh is put into a small, porcelain dish and made into a paste by the addition of distilled water. By means of a polished nickel spatula the mass is shaped into a smooth layer a trifle less than 1 cm. in thickness. The clay is then divided into two portions by cutting a triangular-shaped channel through the mass, the lower edges being separated a little. The dish is then sharply rapped 25 times against the heel of the hand in order to bring about the flowing together of the separated portions. The flow limit has been reached when the two portions of the clay can barely be made to meet at the bottom. If the paste is too thick or too thin, water or clay is added until the proper consistency has been obtained. The water content of the clay mass in this condition is then carefully determined by drying to a constant weight, and the value is expressed as a percentage of the dry weight of the clay. This constitutes the upper or flow limit of the plastic condition; the lower, or rolling limit is to be determined in the following manner. "Clay in the stiff plastic condition is rolled between the hands, and any smooth surface is covered with paper until slender, cylindrical threads form. These 'threads' may break up into smaller lengths, but this is of no significance. Dry clay powder is added to the plastic mass and thoroughly incorporated in it, and the rolling operation is repeated. The desired consistency has been attained when the clay can no longer be fashioned into threads by this method, but crumbles instead. This condition can be recognised without difficulty. The water is determined for this consistency and expressed in terms of

[1] "A Study of the Atterberg Plasticity Method," U.S. Bur. Stands., Tech. Paper, 1915, 46, 3.

the dry weight of the clay. The difference between the moisture contents at the two limits is the required figure."

Drying Shrinkage

The measurement of drying shrinkage is one of the most important tests on raw clays. It is not only of value as an indicator of the range of workability and as a factor which is correlated with nearly all other essential qualities of clay but it is of direct importance, with firing shrinkage, to the manufacturer who requires to make moulds and templates having such an allowance for shrinkage that the finished article is of the required size. According to the Committee on Standards of the American Ceramic Society (1928) the clay should first be thoroughly dried at 64° to 76,° crushed and sieved so as to

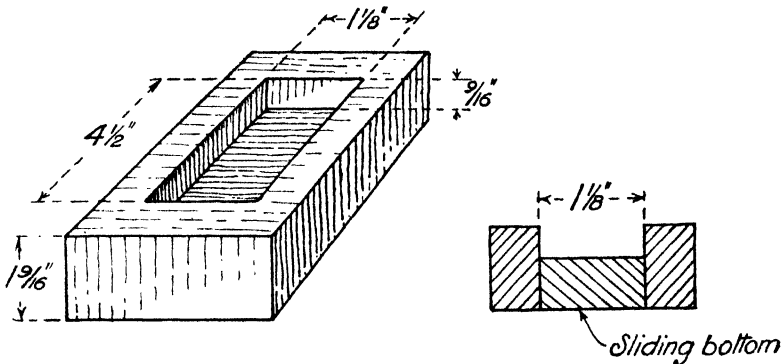



FIG. 12.

pass through a standard 20's sieve, mixed with water to a soft plastic consistency, and thoroughly wedged and kneaded by hand.

For ordinary linear measurements of shrinkage the method recommended by the same committee (1918) is to use a mould as shown in Fig. 12. This gives a test piece $4\frac{1}{2}'' \times 1\frac{1}{8}'' \times \frac{9}{16}.''$ The inside of the mould is first thinly oiled with a rag soaked in paraffin oil. A piece of the prepared clay, rather too large for the mould, is patted into a roll about 4½ in. long and vigorously thrown into the mould so that the clay spreads and fills the lower edges and corners. The remainder of the clay is then worked in to fill up the mould; care should be taken that the fingers are free from oil and that no oiled surface of clay is worked into the test-piece. The excess clay is cut from the top with a stretched wire and the surface smoothed with a rubber slicker or a pallette knife. The surface is then marked with a line having two short lines at right angles to it and about 9 cms. apart. The length between the marks is carefully measured and

recorded before and after drying. (It is convenient to make the marks with a pair of dividers set to the requisite span.) The piece, or preferably two or three similar pieces, is allowed to dry exposed to ordinary room conditions, then at 70° to 80° for four to five hours and finally at 110°. A portion of the same original clay is weighed on a watch-glass and, after drying at 110°, is again weighed. The loss, expressed as a percentage of the dry weight, is reported, together with the shrinkage expressed as a percentage of the wet length. The dry basis for shrinkage data is preferable for some purposes. The appearance of cracks or warping should be noted.

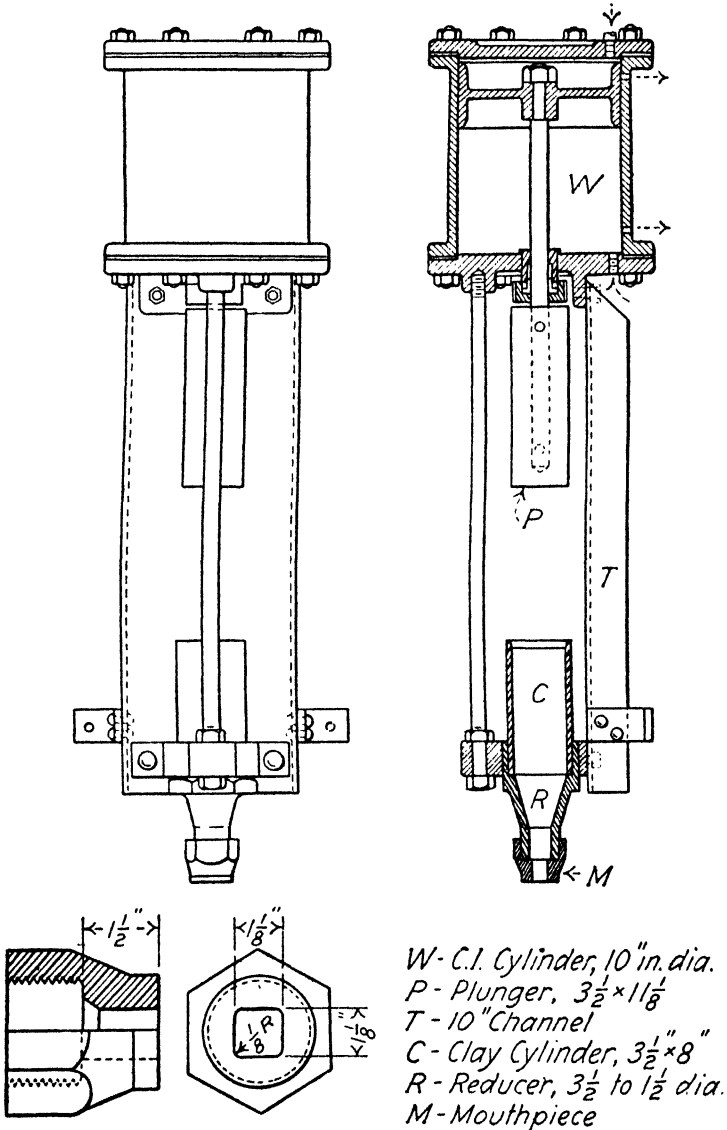
Even under the above conditions the linear shrinkage is liable to vary considerably, and the variation is most marked with highly plastic clays. These irregularities are largely eliminated if the change in superficial volume is measured. For this purpose (1928 Specification, above) a metal mould of 30 mm. by 30 mm. (1⅛ in. square) and any desired length is used. A roll of prepared clay is forced into the mould with the cheek of the fist, using an even layer of paraffin oil or light machine oil as a lubricant; this must not be allowed to get on the hands or work into the clay. The clay bar is taken out of the mould at once and laid, without distortion, on a smooth, straight pallet. It is then cut into lengths of 45 mm. (1⅞ in.). Instead of the mould, a piston plunger-press with a 30 mm. square die may be used. Fig. 13 shows such a press with the essential dimensions. Care is advisable in wedging the clay and in making it into a shape that will fit the extrusion-cylinder without subsequent undue distortion or entrapping of air. With very plastic, sticky clays it may be necessary to substitute for the light machine oil generally used, a heavy oil, or even grease, in the subsequent moulding. Test-pieces should be clearly stamped with a laboratory number.

The volume of the test-piece should be measured to the nearest 0·1 c.c. H. G. Schurecht[1] describes a volumeter of pycnometer type, shown in Fig. 14. The author states that the volumes of 30 to 60 pieces an hour may be determined with this instrument. It consists of a straight-sided bottle 1⅞ in. wide by 5¼ ins. long externally, fitted with an inside-ground centrally-perforated nipple-shaped hollow-blown stopper. The use of paraffin or similar oils involves the determination of the saturated weight (paraffin, S.G. about 0·8) and hence is liable to errors not involved in instruments designed for use with mercury.

An "overflow" volumeter to be used with paraffin oil is also described by Schurecht[2]: this is shown in Figs. 15 and 16. The displacement vessel has a tube passing eccentrically through the base into a 100 c.c. burette. Water-free paraffin is poured into the

[1] *J. Amer. Ceram. Soc.*, 1918, 1, 556.
[2] *J. Amer. Ceram. Soc.*, 1920, 3, 730.

upper vessel, having the stirrup, if any, in place, until the liquid overflows. The burette is then drained and turned off. The test-piece,

FIG. 13.

previously saturated with paraffin if porous, and freed from excess liquid, is then carefully immersed in the displacement vessel and the volume of the paraffin displaced into the burette read off.

A large variety of instruments for the present purpose has been described from time to time; the simplest are often the most useful.

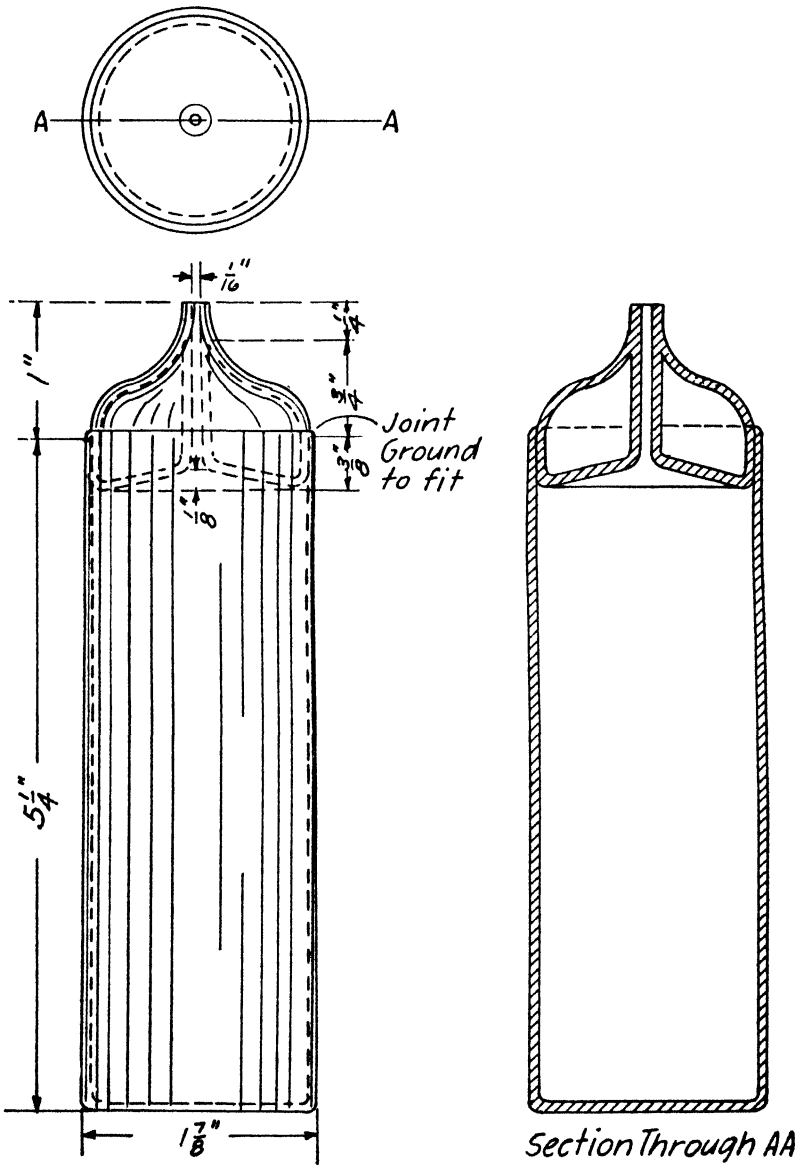



Fig. 14.

Where contamination of the test-piece is especially to be avoided, instruments of the mercury-displacement or the pneumatic type must be used. The latter are generally more suited to the measurement

of porosity, under which heading they are described later. For measurements of the volumes of partially dried clay test-pieces, a simple mercury-displacement apparatus, due to S. R. Hind, is described by R. S. Troop and F. Wheeler.[1] A stout cylindrical glass container having a slightly loose-fitting stopper is filled with pure, clean mercury and stood in a tray. Holding the vessel firmly, the stopper is pressed home and completely rotated. The under side of the stopper should be slightly convex so as to avoid entrapment of air. The displaced mercury is poured off from the tray, any fine globules being brushed up with a soft brush or a clean cloth of fine texture. The test-piece is now forced down into the mercury and the same procedure repeated, except that the displaced mercury is transferred to a weighed dish and weighed. The method proves quite accurate in moderately practised hands, single measurements being sufficient for most purposes. Progressive data on volume and weight, together with the specific gravity of the dry clay, give sufficient data for a complete examination of the progressive development of shrinkage and porosity.

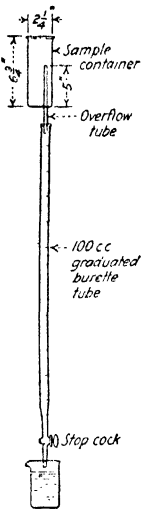



Fig. 15.

Where drying shrinkage only is required the piece may be dried under room conditions until air-dry, then at 64° to 76° for at least five hours, and finally at 110° to an approximately constant weight. For paraffin volumeters, the piece is then soaked in paraffin for at least twelve hours before determination of the volume. The mean of results on two pieces is then reported.

Shrinkage, for systematic purposes, is expressed as a percentage of *dry* volume. The average linear shrinkage (s_L) on the dry basis is derived from the volume shrinkage (s_V) by means of the formula

$$s_L = 100\left[\sqrt[3]{1 + \frac{s_V}{100}} - 1\right]$$

The measurement of the contraction of bodies where casting slip is used presents some difficulty. Slip is poured into plaster moulds which progressively abstract the water from the casting, thus causing it to contract. During the early stages, the adherence of the clay to the mould causes contraction to take place solely in a direction vertical to the surface; but after sufficient hardening has taken place the clay begins to separate from the mould and contract in a more normal manner. The contraction may conveniently be measured by casting trials in a flat-bottomed rectangular mould about 1 in. deep.

[1] *Trans. Ceram. Soc.*, 1928, **27**, 303.

The usual contraction marks are lightly engraved on the bottom of the mould with a sharp knife. The cast piece will show these marks clearly and the contraction on drying can be taken by the usual (linear) procedure.

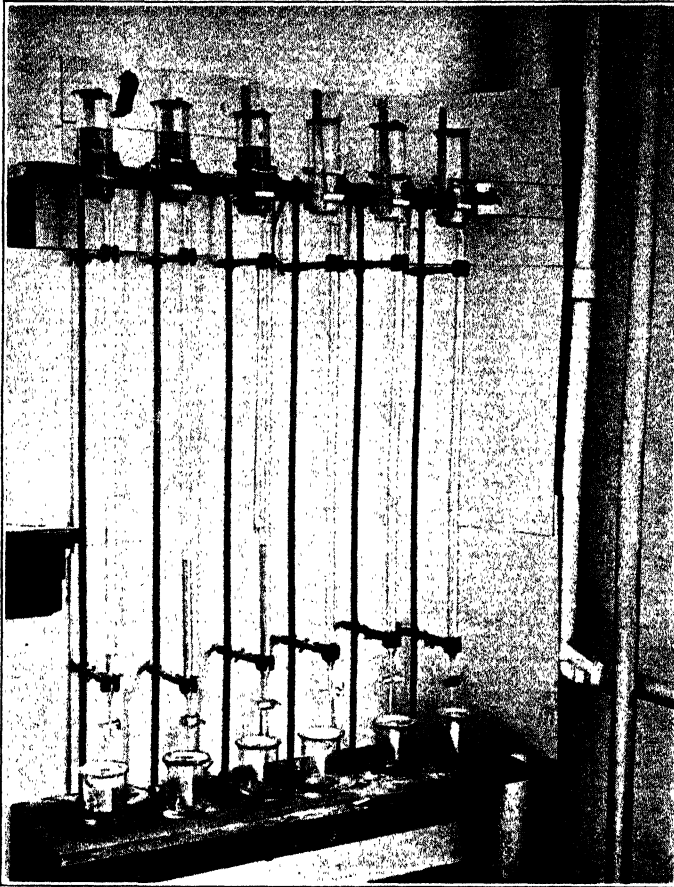



Fig. 16.

Tensile Strength in the Dry State

This is not an easy test to make satisfactorily, but the attempt is justified by its important bearing on manufacture, in particular of ceramic masses having a low proportion of bonding material, as, for instance, with grog bricks, graphite crucibles, and many special refractories. Every care must be taken in the making, drying and breaking of the test-pieces, to avoid the production of irregular strains. The clay must be free from laminations and air-blebs. The drying of fine-grained clays tends to give fine cracks which are not

always obvious at the time, but lead to untimely and erratic results in the testing machine. The method recommended by the committee on Standardisation of Tests for Refractory Materials[1] is as follows.

Making the Test-Piece. A test-piece, similar to that used in cement testing, is made to the dimensions shown in Fig. 17. Plaster moulds are used. The well-prepared and uniform clay is made up with water to a state of maximum plasticity and well wedged by hand.

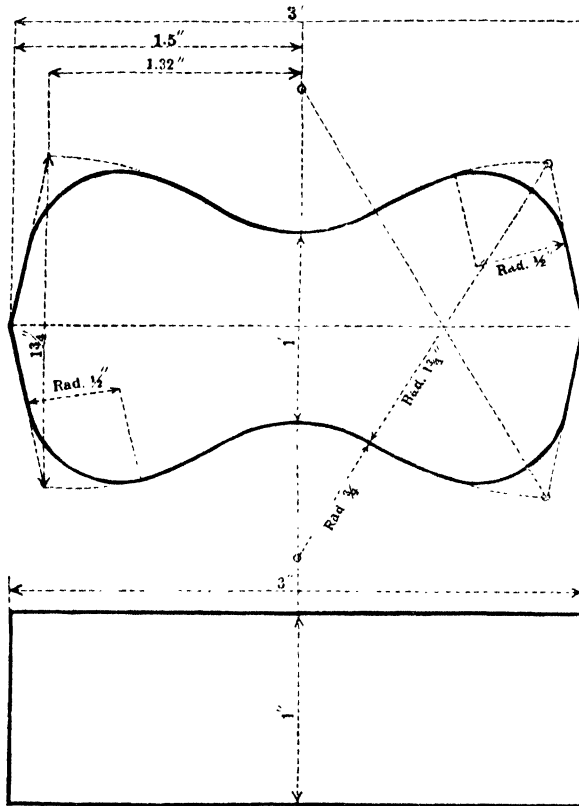



Fig. 17.

It is then moulded, using a regular and uniform pressure. Strong clays and heavily-grogged clays require particular care. The pieces are removed from the moulds as soon as possible and slowly dried under room conditions. (For some experimental purposes it is advisable to complete the drying subsequently at 64° to 76°, followed by drying to approximately constant weight at 110°, and cooling in a closed chamber or desiccator.)

Several machines as used for cement testing are available. A suitable one is shown in Fig. 18. The load is applied by running

[1] J. W. Mellor, *Trans. Ceram. Soc.*, 1918, **17**, 317.

shot into a bucket. The shot container has an automatic cut-off actuated by the fall of the bucket on to a step. The bucket is attached to a long, counterpoised lever, pivoted at a fulcrum so as to move freely between guides in a vertical plane. The primary lever is attached to the secondary lever by means of a combination-screw. A connecting link, swinging near the fulcrum, holds the upper, breaking jaw in position. The lower jaw is connected to a hand-wheel for regulating the distance between the jaws. Roller clips, modified from the standard specification for cement (A.S.T.M.), are

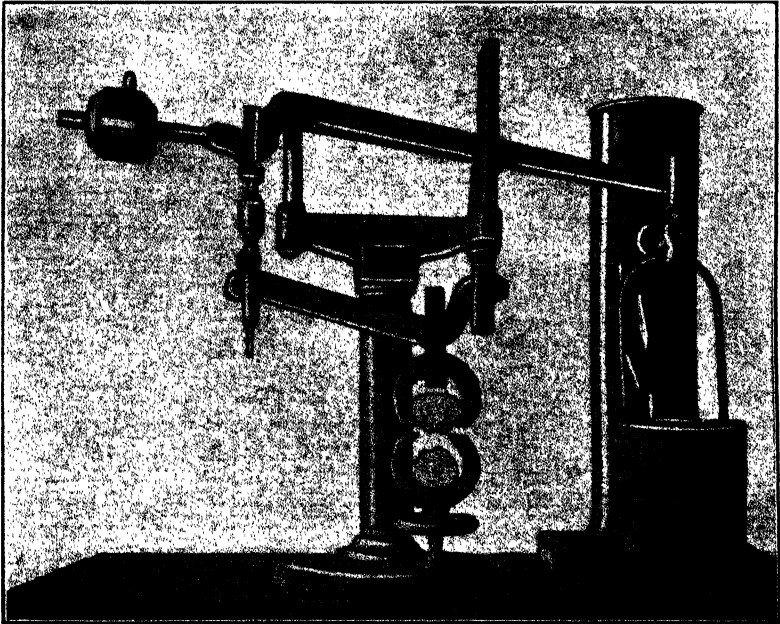
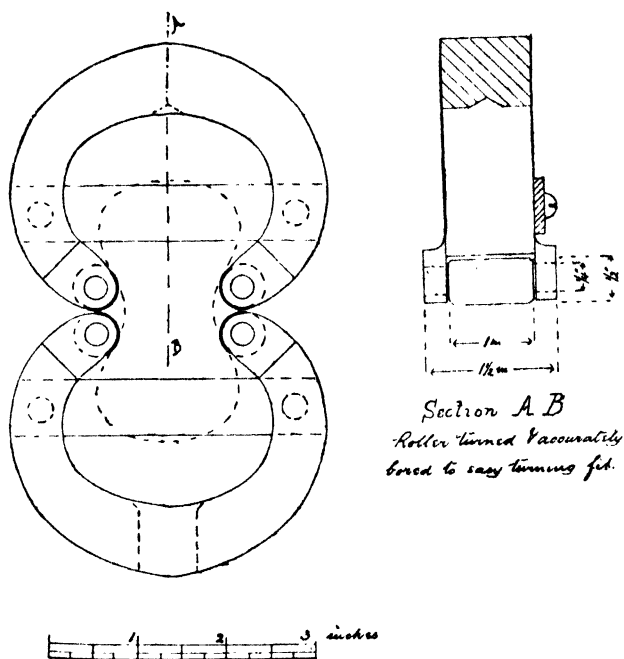



Fig. 18.

shown in Fig. 19. The machine has a total magnification of load, between the shot-bucket and the test-piece, of 50 to 1.

The test is carried out as follows. The primary lever is balanced horizontally, with the bucket suspended, and the test-piece placed in position and carefully centred to give a uniform pull, whilst manipulating the hand-wheel so as to give a light grip. (Pads, consisting of a few layers of blotting-paper, may be inserted between the test-piece and the clips.) A slowly and uniformly increasing load is applied by running shot into the bucket. No shocks must be given, either by irregularly applied load or otherwise. After breaking, the contents of the bucket are weighed (lbs.) and a fresh piece inserted. Pieces showing flaws about the fractured surface, or those which do not break within $\frac{1}{4}$ in. of the middle of the briquette, should be

discarded. The cross-section at the fracture is measured (in.). The tensile strength is calculated by dividing 50 (the ratio of the particular machine) times the weight of the shot by the area of fracture and is expressed in lbs. per sq. in. The average of 5 or 6 tests should be taken for each clay.

Fig. 19.

Transverse Strength in the Dry State

The tentative standard of the American Ceramic Society (1928)[1] is based on the cross-breaking strength of dry test-pieces made with the clay under test mixed with an equal weight of standard silica sand, passing a 20's mesh sieve and retained on a 30's mesh. The clay is first dried thoroughly at 64° to 76°, crushed and screened to pass a 20's sieve. It is then thoroughly mixed with the standard sand and made up with water to a soft plastic consistency and "thoroughly pugged by hand." A suitable metal or wooden mould is used to prepare 10 bars, 17·5 cm. (7 in.) by 2·5 in. square, in the plastic state. The mould should be placed on a firm, smooth surface and evenly and thinly coated inside with paraffin oil. A larger lump of clay than is required to fill the mould is strongly thrown in, so as to fill the bottom corners, the mould evenly filled up, the excess cut off with a spatula, and the surface smoothed off and marked near one end.

[1] *J. Amer. Ceram. Soc.*, 1928, 11, 460.

The pieces are dried under a cloth at room temperature for two days and then exposed to the air until dry, turning them over every twelve hours. They are then further dried at 64° to 76° for at least five days, then at 110° until approximately constant in weight and finally cooled in a desiccator.

A suitable machine (*cf.* p. 368) is used, having two knife-edges 12·5 cm. (5 in.) apart, to support the bar near its ends, a stirrup to load the bar midway between the knife-edges, a receptacle for shot suspended from the stirrup and a means of providing a steady rate of admission of shot into the receptacle, and an automatic cut-off for the supply. The knife-edges should be longer than the width of the test-piece and finished to an edge of 6 mm. (¼ in.) radius. The rate of loading should be about 45 kg. (100 lbs.) per minute. The depth and breadth of the bar are measured at the break to the nearest 0·25 mm. (0·01 in.) and each should be the average of three measurements. The modulus of rupture is calculated from the formula

$$M = \frac{3Pl}{2bd^2},$$

where M is the modulus of rupture, in kg. per sq. cm. (or lbs. per sq. in.); P is the breaking load in kg. (or lb.); l is the knife-edge span in cm. (or in.); b the breath of the bar and d its depth in cm. (or in.). The average of the tests is reported. A variation of ± 15 per cent. from the average is allowable, but if more than two pieces out of the ten have to be discarded the test should be repeated.

III.—THE BEHAVIOUR OF CLAYS IN FIRING

The tests under this heading deal with the most suitable temperature for commercial kiln and oven practice, and secondarily with the ultimate capabilities (*e.g.* refractoriness) and the way in which the important properties such as strength, porosity and colour vary at high temperatures. The latter data are of great value in determining the particular use for which a clay is best suited and, with bodies, in setting the permissible limits of temperature in commercial firing. Thus in certain clays and bodies high in fluxes, particularly lime, the range of vitrification may be so small that, even though perfect ware is obtainable under laboratory conditions, the losses in industrial firing may be serious.

The greater part of British and American firing is carried out under predominantly oxidising conditions and the standard tests which have been devised relate to these conditions. Very different results accrue if all, or specified ranges, of the heating curve are realised under conditions of deficient air supply, such as occur industrially with blue bricks and blue roofing tiles on the one hand and

German hard-paste porcelain on the other. With such materials or bodies, tests should be carried out so as to simulate industrial conditions as closely as possible. The commonest test of all is that largely adopted in works, of firing test-pieces of raw materials and new bodies, etc., in various parts of the ovens and kilns along with the ware. Such a method is of great value for the control of materials, but is restricted in its usefulness to the class of ware actually being produced. The standard methods of testing give far more information, but even then it is advisable, particularly in the case of bodies, after having carried out these tests to send further trials through industrial kilns which provide the conditions which the earlier tests have indicated to be suitable.

The ordinary analytical procedure provides the necessary information as to hygroscopic water (driven off up to 110°), combined water (removed over part of the range 110° to 800°) and carbonaceous matter (oxidised between 300° and 900°) (*cf.* pp. 10-12). The actual temperature-ranges over which the various losses take place vary to a considerable extent with the material and such conditions as size of ware, size of kiln, rate of heating and ventilation of the kiln. In addition, the changes in accessary minerals such as pyrites, marcasite and other sulphides to sulphates, sulphites, lower sulphides, metal (*e.g.* iron) and oxides; carbonates to oxides, as of calcium, magnesium and iron; and of oxides, such as ferrous and ferric oxides and magnetite amongst themselves, are also taking place in various stages of the firing. These changes are not, at present, the subject of ordinary tests; a good account of them is given in text-books of ceramics, of which that by H. Wilson [1] is to be recommended.

The standard tests of behaviour in firing are concerned with the properties of samples after heating in a specified manner to specified temperatures, as controlled by a series of Seger cones (p. 84). Ceramics being concerned with only partially completed changes, time is a vital factor, as well as temperature, in determining the state of fired ware. This factor is automatically included in the indication of ceramic trials, such as Seger cones, contraction-rings, etc., and the results of laboratory trials with comparatively rapid heating are therefore the more readily applied to the industrial conditions; also, the cones are frequently of value as a simple control over the regularity of heating, and their use tends to counteract differences in rate of heating between different tests. The object of the tests is to study progressive changes in porosity, volume, true specific gravity, mechanical strength, colour, hardness and related properties.

Test-pieces, as used for drying shrinkage, of which the dry volume or the length on contraction-marks is known, are set in a muffle, of which the walls are as thin as possible, placed in the test-kiln. The

[1] *Ceramics—Clay Technology*, M Graw Hill, 1927.

pieces should not be too close together, and should be suitable in number and arrangement for the drawing of trials at each of the stages indicated below. The effective space of the kiln should be greater than 2 cub. ft. (English Specification) or not less than 1½ cub. ft. (American). A set of Seger cones is to be placed as close up as possible to the test-pieces, and a platinum, platinum-rhodium thermocouple with a standard cold junction, arranged conveniently for taking the temperature of the pieces. During the first few firings, the temperature distribution should be explored with this couple. The American Specification for rate of heating is 45° ± 15° per hour from the start up to the third cone below that at which trials start being drawn, and 20° ± 5° per hour from then on. The following ranges of cones and starting points for drawing trials are recommended:—

Impure, common brick clays . . .	014 to 3;	draw at 010
Shales and better types of ferruginous clay	012½ " 5;	" 08
Clays of fireclay type	02 " 15;	" 2

A test-piece is subsequently drawn at each two-cone interval, recording the temperature before each drawing. The pieces should be drawn as quickly as possible, and the loss of heat made up by temporarily altering the controls of the furnace.

The English (Ceramic Society) Specification is different in detail. Solid, gaseous or oil fuel may be used. The rate of heating should not exceed five cones or 100° per hour until 900°, or cone 010A, is reached, after which the rate should be one cone per hour throughout. (The cones specified here are those marked with the Staffordshire Knot; the American cones are made by Ed. Orton, jr.) A thermocouple pyrometer should be used to check fluctuations. For low-grade clays, trials are to be drawn at cones 010A (900°), 08A (940°), 05A (1000°), 02A (1060°), 1A (1100°), 4A (1160°), 6A (1200°); for higher-grade clays, at cones 010A (900°), 05A (1000°), 1A (1100°), 4A (1160°), 6A (1200°), 8 (1250°) and 10 (1300°). If desired, drawings can be carried on up to cones 12 (1350°), 14 (1410°) and 16 (1460°). The test-pieces, as removed, should be covered with hot sand and kept at about 700° in an auxiliary furnace until all are drawn, after which they are allowed to cool at the rate of the furnace. (The temperatures given above as corresponding to the cones are nominal, corresponding to the results of heating under standard conditions.)

When cool enough, the pieces should be transferred to a desiccator containing conc. sulphuric acid and left till cold. The pieces should be freed from any adhering particles of sand, etc., and weighed to the nearest 0·1 g. Where linear contraction-marks are in use, the length should be measured and recorded, and the dry-to-fired contraction calculated as a percentage of dry length. The tests to be carried out on the fired test-pieces are described later; for these, see

Examination of Fired Clays, p. 93. Colour changes should be noted in the usual qualitative manner. (For special purposes the Lovibond[1] or other colorimeter or a standard colour-chart may be used.) For a general indication of hardness, samples are scratched or cut with a steel knife and the result noted.

It is advisable to plot the results of each test in the form of a graph, against cones as heat units. Equal scale units should be taken to represent two cones and 5 per cent. porosity on the abscissæ and ordinates respectively. The corresponding temperatures should be noted under each cone number.

Thermal Expansion

The change in size which is due to the heating of the test-piece, and which disappears on cooling, is here indicated. It is the normal, reversible expansion, or a coefficient expressing the difference between

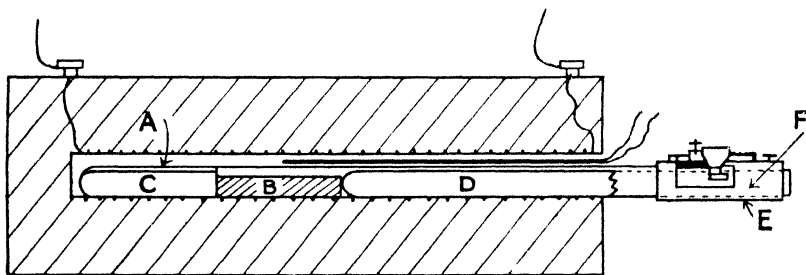



FIG. 20.

hot and cold sizes. Permanent changes which have come about through heat treatment are usually studied on the cooled test-pieces (*e.g.* changes in porosity, volume and strength). It must be borne in mind where unfired test-pieces, or pieces not fired at temperatures considerably beyond the limits adopted in the present test, are used, that such permanent changes are super-added to the ordinary expansion. The two effects may generally be separated by taking data during cooling as well as heating, repeat tests, or making the compensating outer tube, if any, of the pre-fired material. This test has, so far, been largely used in examining fired and partially fired samples of refractory materials.

The apparatus of H. J. Hodsman and J. W. Cobb[2] is shown in Fig. 20. The furnace is an electrically heated fireclay tube 18 in. long, closed at one end by a fireclay plate. The tube is wound with nichrome wire, the pitch of which is reduced towards the ends so as

[1] J. W. Lovibond, *Trans. Ceram. Soc.*, 1910, **10**, 66; *cf.* K. S. Gibson and F. K. Kraus, *Bur. Stand. Sci. Papers*, No. 547, 1928. [2] *J. Soc. Glass Tech.*, 1919, **3**, 201.

to compensate for the greater rate of heat loss and ensure a long zone of constant temperature. The winding is plastered with fireclay paste, dried, and the whole placed axially in a shell of tinplate filled with light magnesia. The current is regulated by resistances in series and in parallel, 7 amps. at 200 volts being required to maintain the maximum temperature of 1000°. The furnace tube is placed horizontally. It contains a fused silica tube, A, 3·8 cm. in diameter and 50 cm. long, with its open end projecting and having a brass tube, E, attached. The specimen, B, usually about 20 cm. by 2·5 cm., is placed inside between distance-pieces C and D of fused silica, so as to bring the test-piece into the zone of uniform temperature. To the distance-piece D is cemented another brass tube, F, sliding within the tube E between guiding screws and permitting a circulation of air between the two. (The whole train of parts inside the tube A should be lightly pressed inwards so as to maintain contact.) Both brass tubes have attached to them glass plates lying closely one over the other and carrying fine parallel scratches. The scratches are observed through a microscope fitted with a micrometer eye-piece, and the distance between them measured at different temperatures. In the original apparatus, one division of the eye-piece scale corresponded with 1114×10^{-6} mm. The temperatures are observed by means of a platinum, platinum-rhodium thermocouple attached to the outer silica tube, the junction being about the middle of the specimen. The measurements are, of course, relative to the coefficient of expansion of silica, which is known with some precision. The data of G. W. C. Kaye[1] may be used, as follow :—

0° to 30°	42×10^{-8}
30° „ 100°	53×10^{-8}
100° „ 500°	58×10^{-8}
500° „ 900°	50×10^{-8}
900° „ 1000°	80×10^{-8}

The temperature is normally raised at the rate of 130° per hour.

The apparatus specified by the American Ceramic Society[2] adopts the vertical position for the train containing the test-piece, uses kieselguhr as insulating material, measures the expansions with an "Ames" dial and omits the compensating outer tube, thereby facilitating the placing of the tip of the thermocouple close to the base of the test-piece ($6 \times 1 \times 1$ cubic in.). The temperature of any part of the specimen may readily be explored by raising the couple. A potentiometer is used with the couple. The whole apparatus is calibrated with a well-annealed bar of fused silica in place of the specimen.

[1] *Phil. Mag.*, 1910 (vi), **20**, 718.

[2] Anon., *J. Amer. Ceram. Soc.*, 1928, 522 ; *ibid.*, 1927, **10**, 569.

Any required temperature may be maintained constant for twenty minutes by means of a rheostat, before taking a reading. The readings are corrected for the expansion of the base and rod as found from the calibration. An average linear coefficient may be calculated by dividing the change of length per unit length by the change in temperature. Starting at atmospheric temperature and plotting the percentage elongation against the temperature gives a graph which is generally more useful than a statement of the average coefficient over the whole range or a series of ranges.

A test with a similar object, designed to give direct readings of change of length on a whole firebrick is given later (see p. 127). The above apparatus may, of course, be used with specimens cut from finished clay goods.

F. H. Norton[1] describes another rather similar method, in which the change of length is directly read by telescopes against a brilliantly illuminated screen. Using natural gas and a premixing burner, he had no difficulty in carrying his tests up to 1700° on a variety of materials.

Thermal expansion under load is directly given by the data of the Refractoriness-under-load Test (see p. 89), providing the apparatus has been calibrated against a known material, such as a special carborundum block, and allowance made for the supports, etc.

Sag Tests

These tests are sometimes used for pottery materials; as a basis of comparison, the behaviour of standard materials under the same conditions is observed. In such cases it is usual to fire the test-pieces in a separate saggar in the biscuit oven. The test is enlarged in scope in the following tentative testing method of the American Ceramic Society.[2] In this form it may occasionally be of value for testing refractory materials. (See also Refractoriness under Load, p. 89.)

The general method is to support a bar, made up from the required raw material, on refractory knife-edges and fire up as previously indicated (p. 78), drawing trials at two-cone intervals. The bar may be loaded at the middle as indicated below. The amount of sagging is determined in duplicate on at least five heat treatments at successive temperature intervals. The amount of sag at the centre of the bar is measured to the nearest 0·1 mm. and divided by the distance between the knife-edges. The result is called a warpage-ratio. The specification distinguishes between *fine grog bodies*, where all the non-plastic material passes a 20's sieve, and *coarse grog bodies*, in

[1] *J. Amer. Ceram. Soc.*, 1925, 8, 799. [2] *Ibid.*, 1928, 11, 458.

which any of the grog remains on a 20's sieve. The following conditions are recommended :—

	Fine-grogged.	Coarse-grogged.
Thickness	12 mm. (½ in.)	65 mm. (2½ in.)
Width (horizontal) . .	25 mm. (1 in.)	65 mm. (2½ in.)
Length	230 mm. (9 in.)	330 mm. (13 in.)
Knife-edge clearance . .	177 mm. (7 in.)	255 mm. (10 in.)
Allowance in cross-section .	Scraped or rubbed true	± 3 mm. (± ⅛ in.)
State at commencement of test	Unfired ; thoroughly dry	Fired to at least one cone above test-range
Load	None added	4·5 kg. (10 lb.) when exactly to size.*

* Otherwise, within 3 mm. limits, load = $0·0185\ b\ d^2$, in kg., b and d being measured in mm., or $0·64\ b\ d^2$, the units being lb. and in.

The fine-grogged bodies are made into a slip of suitable consistency and cast in plaster moulds to a thickness of just over 12 mm. in the dry state, dried to "leather-hard," cut into strips just over 25 mm. wide and longer than 230 mm., allowing for subsequent shrinkage in drying. The pieces are then dried thoroughly and finished true to size. The knife-edges used should be triangular in section and 45 mm. (1¾ in.) high.

The coarse-grogged bodies are made up to soft-plastic consistency with water, pressed in a suitable mould, first throwing clay to the centre and two ends of the mould and filling the lower corners; the mould is then filled up and excess clay struck off with a wire, the piece smoothed off and marked. It is subsequently dried and fired to at least one cone beyond the test-range adopted, in such a way that no warping occurs. The "knife-edges" recommended in this case are flat fireclay supports. The load is applied at the centre by means of a fireclay stirrup with a knife-edge support.

In reporting the results, variations of over 20 per cent. from the average should be rejected.

Normal Refractoriness of Fireclays, Bodies and Finished Ware

In this test a slender tetrahedron ("cone"), with its upper face inclined at an angle of 82° to the horizontal, is heated to such a temperature that partial or total fusion causes it to soften and bend over. The critical point is reached when the tip of the cone has bent over so as to be on a level with its base.[1] The test consists in making a comparison with standard pyrometric cones. The nominal temperatures of squatting of English cones correspond with those of the German Seger cones (New Series) and are given in the following table. For convenience, the corresponding numbers of

[1] In the English test this applies only to the standard cones. The sample under test is required to show definite softening, which usually corresponds to having the tip bent "half over."

Watkin recorders and Holdcroft bars are also given. These latter trials, together with Seger cones, Wedgwood pieces, Contraction rings and various colour draw-trials are variously used in works practice for the control of firing. With the exception of those given in the table, it is not thought advisable to indicate definite temperature equivalents. The nature of some of them is varied considerably to suit different requirements and they are usually calibrated against a desired state in the finished ware. Sometimes they are actually constituted of the same material as the body, glaze, or decoration of the ware.

Squatting Temperatures of Seger Cones, etc.

Degrees Cent.	Seger Cone No.	Watkin Record No.	Bar No.
2000	42	59	...
1960	41	58	...
1920	40	57	...
1880	39	56	...
1850	38	55	...
1825	37	54	...
1790	36	53	...
1770	35	52	...
1750	34	51	...
1730	33	50	...
1710	32	49	...
1690	31	48	...
1670	30	47	...
1650	29	46	...
1630	28	45	...
1610	27	44	...
1580	26	43	...
1550	...	...	40
1535	...	...	39
1530	20	42	...
1520	19	41	38
1505	...	...	37
1500	18	40	...
1490	...	...	36
1480	17	39	...
1475	...	...	35
1460	16	38	34
1435	15	37	...
1410	14	36	33
1380	13	35	32
1350	12	34	31
1325	...	...	30
1320	11	33	...
1300	10	32	29
1280	9	31	28
1270	...	...	27A
1250	8	30	27
1230	7	29	26A
1200	6A	28	26
1180	5A	27	...
1160	4A	26	...
1140	3A	25	25
1120	2A	24	24
1100	1A	23	23
1080	01A	22	22
1060	02A	21	21
1040	03A	20	20
1020	04A	19	...
1000	05A	18	19
985	...	...	18
980	06A	17	...
970	...	...	17
960	07A	16	16
950	...	...	15
940	08A	15	...
935	...	...	14
920	09A	14	13
905	...	...	12
900	010A	13	...
890	...	...	11
880	011A	12	...
875	...	...	10
860	...	...	9
855	012A	11	...
840	...	...	8
835	013A	10	...
815	014A	9	...
810	...	...	7A
790	015A	8	7
760	...	...	6
750	016	7	...
730	017	6	5
710	018	5	...
700	...	...	4
690	019	4	...
670	020	3	3
650	021	2	2
600	022	1	1

The Seger cone temperatures are stated to be correct when the time of heating, up to bending, is from two to six hours. Longer times give lower temperatures, and shorter times, higher temperatures. Watkin recorders consist of small pellets of the same mixtures as Seger cones, set in a fired plaque having a numbered hole for each pellet; the plaques usually hold five pellets covering a 10-cone range. The critical indication is given by a pellet fusing into its cup, so that it just cannot be removed.

Holdcroft bars are composed of similar ceramic mixtures and are supported near their ends on a fireclay rack stepped down to the front, so that a clear view of all the pieces is possible when the set is placed in the oven or kiln. The bars softening at lower temperatures are set on the lower steps. The sagging of the bars is noted as the firing increases and the sagging thus ⁄⁀⁀\ indicates the critical condition; a simple bend at the middle of the bars is not sufficient. The use of all these ceramic heat trials requires care and some practice in order to obtain consistent results. They may also be affected by accumulations of carbon or flue dust, and for this reason are best protected in various ways indicated in text-books on ceramics, or by the makers.

The preparation of test-pieces for refractoriness varies with the material. When a clay, or any sample whose existing structure may be destroyed, is to be tested, the material should be sampled carefully as for a chemical analysis. If need be, it may be crushed by a hardened steel pestle and mortar, afterwards removing the iron magnetically (so long as the original sample was known to contain none). It should then be ground to pass a 60's sieve without undue production of fine powder. The dust is made up into a stiff paste with water, adding gum or glue if necessary, and formed into cones. According to the American Ceramic Society's Standard Specification (1928) the above method of preparation is to be applied invariably, whereas the English Committee's method (1917) indicates that representative pieces of *fired* goods to be tested should be chipped or shaped into a cone about 1½ in. high, and it is, in practice, customary to grind the pieces to shape on a carborundum or emery wheel. The American specification is to mould, in steel moulds, tetrahedra ("cones"), having 7 mm. base edges and a height of 30 mm. The test-pieces are trimmed down when dry and may, if desired, be biscuited at a low temperature. (A temperature of 400° to 600° is satisfactory with clays.) The pieces are then mounted on an unfired refractory plaque (*e.g.* equal parts of a highly refractory clay and fused alumina both ground to pass a 100's sieve). A small quantity of the same mixture in slip form serves for cementing, but the insertion of the cone must not be more than 2 mm. The trowelled and badged

face of the cone should have a slope of 82° to the plaque. Test-pieces are mounted alternately around the plaque with a series of standard cones of successive numbers to suit the material under test. The plaque and cones may be biscuited before testing. The furnace used should preferably give a neutral or oxidising atmosphere and be frequently explored for uneven heating. With gas or oil fuel, the flame must not impinge directly on the assembly under test. The following successive times of heating are recommended:—

To cone 20,	45 mins.	To cone 30,	4 mins.
" " 23,	20 "	" " 31,	8 "
" " 26,	6 "	" " 32,	4 "
" " 27,	4 "	" " 33,	8 "
" " 28,	4 "	" " 34,	18 "
" " 29,	10 "	" " 35,	6 "

At 1000°, a used cone-pat may be replaced by a new without cooling the furnace below red heat. Intermediate values are to be reported as in "cone 31 to 32." If a lengthy softening range, or bloating, squatting or unequal fusion are observed, these should be reported. Two or more tests should be carried out.

The above specification is, in the author's opinion, so full of minute and rather inconsequential detail, that it is doubtful whether it will, in practice, be strictly followed.

A suitable gas-fired furnace is that designed at the Mellon Institute.[1] Gas is used under a pressure of 4 oz. and at 6 lb. (per sq. in.). The air pressure is reduced from that of a supply at 25 lb. per sq. in.; an equalising tank of 100 gal. capacity is recommended.

Alternatively,[2] a platinum - wound electrical resistance furnace with a chromel "booster coil" may be used. This is an attractive design having an inner platinum-rhodium wound alundum tube and an outer winding of chromel wire which relieves the inner winding of a great part of the load. The outer winding must, however, be carefully kept at a temperature well below 1200°. Around the coils is an ample insulation of Sil-o-Cel and a steel outer shell. The inner tube, which constitutes the working chamber, is protected at its ends by means of two series of refractory boxes, perforated in the one series to pass a thermocouple, and in the other having mica windows down the axis of the tube. Full details and drawings, together with a performance record, etc., will be found in the original paper.

In English practice it is customary to mount test-pieces, prepared as already indicated, on a pre-fired plaque of the composition given, or containing sillimanite, using a paste of similar composition for mounting. The specimen cone is mounted centrally and surrounded by a ring of standard small-size cones, chosen according to the

[1] Anon., *J. Amer. Ceram. Soc.*, 1928, 11, 529. [2] *Ibid.*, 530.

material tested. The cones are slightly sloped outwards, with the badged face inwards. The prepared disc and cones are placed on the lifting table of a Hirsch or similar electrical furnace. Fig. 21 shows a suitable furnace. The temperature is raised at about 50° per five minutes until the first cone begins to melt; an initial energy of 2 to 3 kw. is suitable, and a transformer or resistance control (or both) is used, preferably with alternating current. Successive cones should melt at not less than five-minute intervals, as too rapid heating makes the refractoriness appear unduly high. "The temperature at which the test-piece bends over, squats or shows signs of fusion is taken as the softening point," as judged by comparison with the standard cones. Finally, the current is switched off, the support lowered and the disc and the cones plunged into cold water, a procedure which prevents the piece breaking up on cooling. When considerable doubt exists as to the refractoriness of a sample, 2- or 4-cone intervals for the standard cones are used in a preliminary test.

The Deformation-Temperature of Enamels

This method[1] is applicable to frits and milled enamels. A fair sample of the material is thoroughly dried, ground in a porcelain pebble mill to pass a No. 150 sieve. Cones ⅝ in. on base edges and 2½ in. high are moulded from the powder mixed with sufficient water and organic binder to give the necessary plasticity and cohesion. The pieces are removed from the moulds and well dried. They are then mounted on a plaque of asbestos board or a strip of enamelled steel sheet, using a plastic mixture such as sand, clay and water and placing the trowelled faces of the pieces at an angle of 82° to the plaque. Two pieces are placed facing the same way so that the end of a thermocouple may be located in the air mid-way between their tips and ½ in. below them. The thermocouple is inserted in the furnace so that its tip lies 1 in. or more below the top of the furnace and about in the centre of its horizontal plane. The cone plaque is thoroughly dried and packed up in the correct position, the furnace being at not over 800° F. The pyrometer should control the temperature, between 800° and 1600° F. to plus or minus 5° F. A 10° F. range has been suggested as adequate. The rate of heating above 800° F. is recommended to be as follows:—To 1020° F. in ten minutes, to 1150° in twenty minutes, to 1260° in thirty minutes, and to 1370° in forty minutes. For each piece, the initial bending and final bending, such that the *tip is level with the base*, are observed. The first is recorded as the "starting temperature," the second as the "deformation temperature" and the difference as the "deformation range." Two or more close checks should be averaged for the final result.

[1] *J. Amer. Ceram. Soc.*, 1928, **11**, 465; *Bull.*, 1927, **6**, 259.

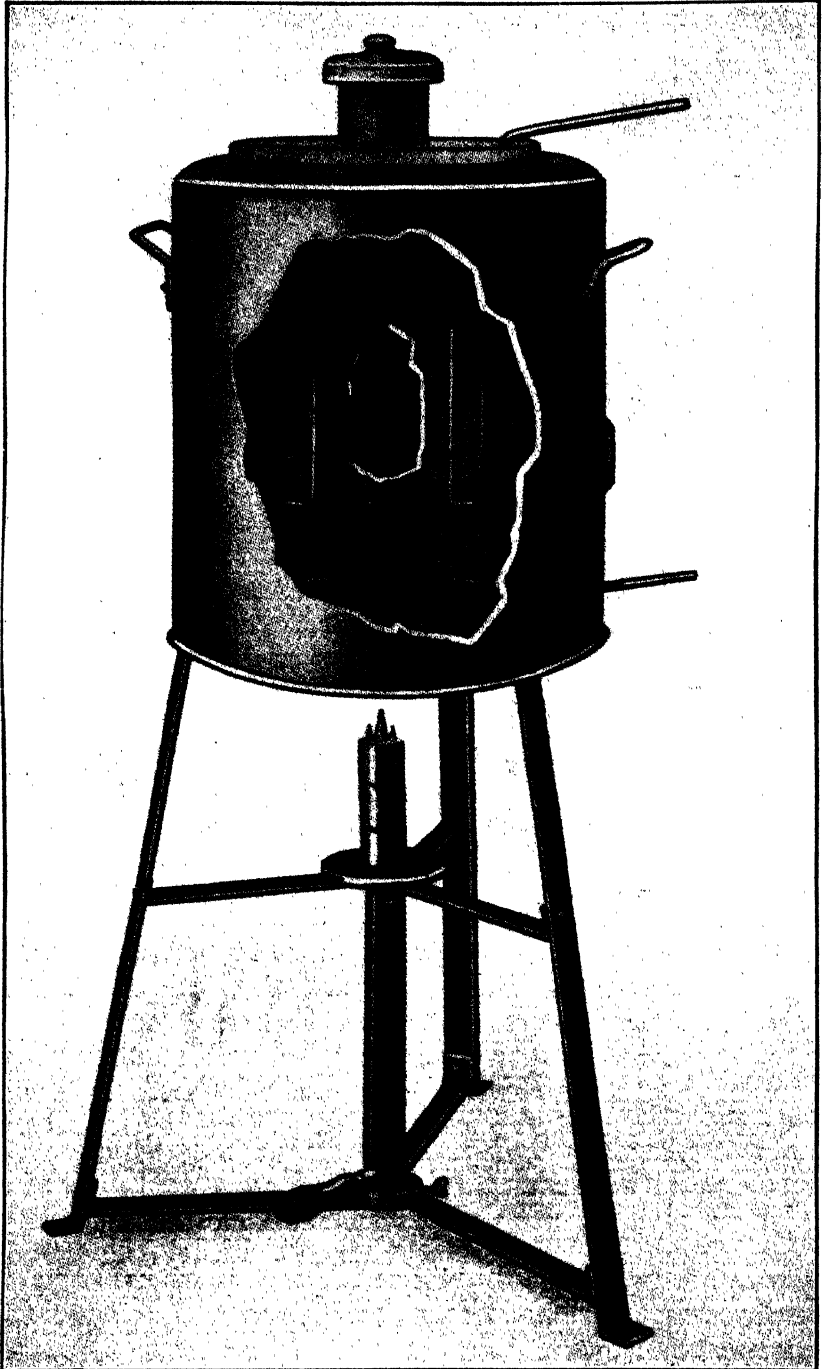



FIG. 21.

Test of Refractoriness under Load

This method has been the subject of considerable inquiry and improvement in detail since the original suggestions of J. W. Mellor and B. Moore.[1] The test was devised because it was realised that the load-bearing capabilities required of most refractories in service were frequently overstepped, and the normal refractoriness had given no

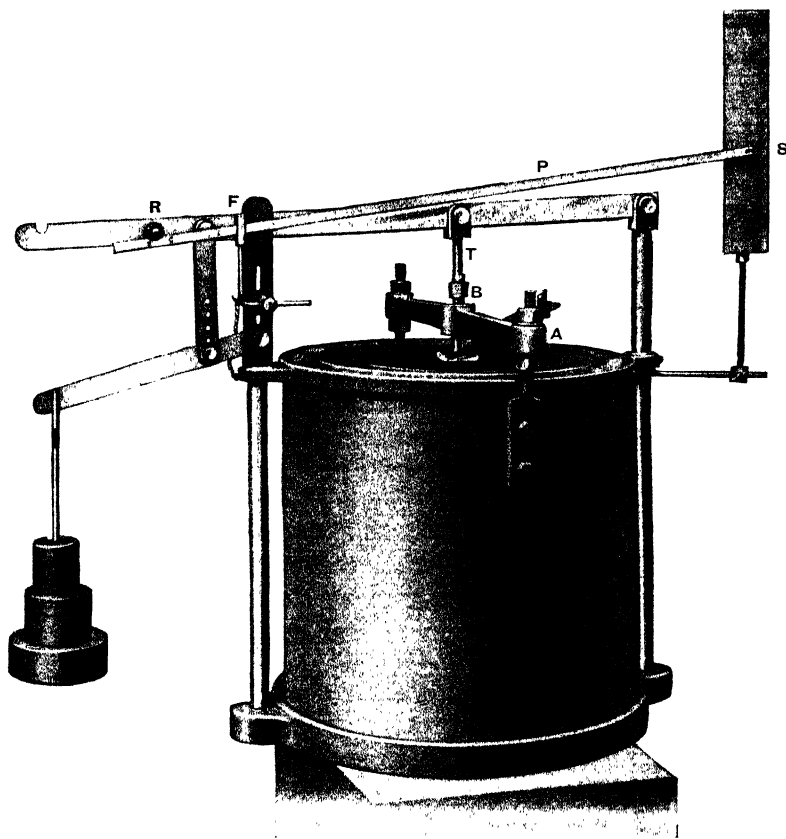



Fig. 22.

indication of the behaviour under load. Industrial conditions and refractories vary to such an extent that materials may sometimes safely be used in furnaces at temperatures higher than the normal squatting temperature, whilst in other circumstances the refractory, when subjected to loading, fails at a much lower temperature than the normal refractoriness would indicate. A test was therefore devised in which the material was subjected to conditions which more nearly represented its service-

[1] J. W. Mellor and B. Moore, *Trans. Ceram. Soc.*, 1915, 15, 117; J. W. Mellor and W. Emery, *ibid.*, 1917, 17, 360.

ability under industrial conditions. Care must still, however, be used in discriminating between the standard conditions of the test and the actual conditions of the service in view. It is, for example, obvious that a fireclay refractory will give better service when built into the wall of a furnace cooled on one side than, say, when it forms an isolated pillar, all the sides of which are subjected to the furnace temperature. In the former structure it is clear that the initial effects of the load will be to cause sufficient strain in the softened surface layer of the refractory for a more or less complete transference of the load to the cooler and more rigid structure behind it. Such could not, for long, occur with the pillar. Further, neutral or oxidising atmosphere is aimed at during the test, while other conditions more favourable to fusion and destruction of refractories are frequently found in practice. Possibly these factors will be taken into account in future testing methods.

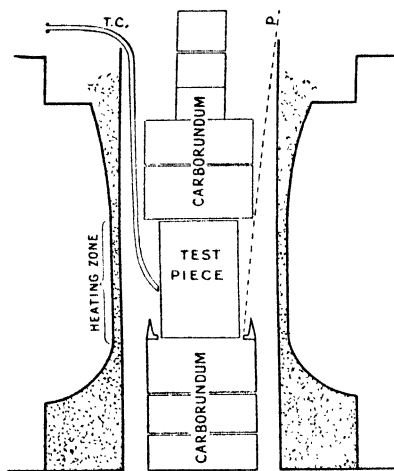



FIG. 23.

The following account of the load-test is substantially that given by A. J. Dale.[1] The furnace and loading arrangements are shown in Fig. 22, and the details in the heating zone of the furnace in Fig. 23. The furnace is essentially that used by J. W. Mellor and B. Moore[2] and the size of the test-piece that adopted by J. W. Mellor and W. Emery[3] (*i.e.* 3½ in. high × 2 in. × 2 in., with ends ground smooth and parallel). Heat is developed electrically in the granular carbon resistor, its development being specially localised in the neighbourhood of the test-piece. The carbon is confined between a special refractory lining and a tubular fireclay section, preferably slip-cast in two parts from, say, an 80/20 sillimanite-clay mixture. Outside this, insulation may be inserted to protect the steel case. Alternating current supply feeds a stationary transformer having a tapped secondary winding giving a voltage range of 60 to 110 in approximately 5-volt steps. A variable external resistance of carbon plates or a wire-wound resistance with an ammeter completes the equipment and allows of fine control of the heating. With a maximum consumption of 20 to 30 kw.-hours, a temperature at the face of the test-piece of 1700° is obtained. A standard rate of heating of 50° per five minutes is maintained throughout the test until a subsidence of ½ in. has been registered. The temperature at which this occurs,

[1] *Trans. Ceram. Soc.*, 1928, **27**, 22. [2] *Ibid.*, 1915, **15**, 117. [3] *Ibid.*, 1917, **17**, 360.

under a load of 50 lb. per sq. in., is taken as the temperature of failure under load. For special purposes the heating may be arrested at a specified temperature (*e.g.* 1350°) and the subsequent progress of the subsidence observed at the three- or five-minute intervals previously adopted for the heating curve. The results should be plotted directly with scale-readings as ordinates (noting the magnification, generally 16 to 1), and with temperatures as abscissæ. Where the temperature is arrested at a given point, the graph is conveniently continued with time (hours) as abscissæ, starting from zero at the point where the temperature rise ceased. Other peculiarities of the behaviour of the specimen should be carefully noted; a photograph of the test-piece is often very informative. The load is applied to the column containing the specimen by means of a thrust rod T (Fig. 22) which passes through a hole drilled in a cross-bar A. The latter is so mounted that it may be readily adjusted so as to maintain the thrust-rod in a vertical position. To the rod is attached the cup of the cup-and-ball arrangement B, which eliminates the side-thrust developed by the descent of the main lever above it. The load is transmitted to the piece by means of this lever and the secondary lever shown on the left of the figure. This train of levers is calibrated so as to give the desired load on the standard test-piece. A graduated, notched aluminium rod P, 42 in. long, serves as an indicator of the movement of the system. It is actuated by a projection R, on the primary lever, supported on a movable fulcrum F, and indicates on a scale S. The end of the indicator lever is cut out U-shaped and has cross-wires fixed in the "U." The ratio of magnification from the test-piece to the scale may be varied from 10 : 1 to 40 : 1 at will, whilst a magnification of 16 is usually employed. The indications on the scale may be recorded automatically by the addition of a pen and clock-driven drum.

The test-piece is supported on pressed carborundum blocks so much greater in section than the test-piece that there is room for a set of test-cones as a check on the ultimate temperature. The piece is supported in the zone of maximum temperature. It is capped by more blocks of carborundum and finally by cylinders which carry the column up to a convenient height for contact with the thrust-rod. In setting up the column the greatest care is required in starting from a level base and levelling the top of each piece as it is placed in position. The whole column must also be correctly centred: the test-piece is protected by these precautions from uneven loading. The temperature readings are taken with a platinum, platinum-rhodium thermocouple whose hot junction just touches the centre of one side of the test-piece, and with an optical pyrometer of the disappearing filament type. The couple is in use up to 1250° and the optical pyrometer from about 800°

to the finish. The optical pyrometer is focussed between the cones on the cone-plaque, as indicated in Fig. 23 by the dotted line. During the period that both pyrometers are in use the readings should check to within 10°.

Care must be taken to maintain an even temperature in the hot zone; this largely depends on skilful control of the granular resistance in which the heat is generated. There is a tendency to arcing, leading to a local rise of temperature and still greater flow of current. When this is noticeable, or before, the carbon should be gently disturbed with a long pointed iron wire, so as to fill up any cavities due to oxidation or subsidence of the carbon.

On the completion of the test, the current is switched off and the furnace and contents left to cool. The state of the test-piece and of the cones is then noted. The change of length of the test-piece may be corrected for end effects due to the supports by calibration with a block of material (such as that used for the supports) in a preliminary run of the furnace.

Mellor noted that when cone 16 had been reached in about four hours the difference between interior and exterior temperature of the test-piece was still about 20°; from this fact it was argued that it would be undesirable to base the test on the behaviour of a whole brick. Such a standard has, however, been adopted in America (A.S.T.M., Ser. Desig. C 16-20[1]). The difficulty has been surmounted by utilising a time of heating which, for 1460°, is more than twice as long as that recommended in the British test.

The American specification divides material for testing into four categories, and specifies a certain temperature which shall be reached by a given time-temperature schedule in 6 hours (silica), otherwise in 4½ hours, to be followed by a period of 2 hours (silica), or 1½ hours (other classes) during which the temperature is maintained constant. Thus, the limits are:—

Silica	to 1500° C. in 6	hours, plus 2	hours stationary
Heavy-duty fireclay .	to 1350° C. in 4½	,,	1½	,,
Moderate-duty fireclay .	to 1300° C. in 4½	,,	1½	,,
Light-duty fireclay. .	to 1100° C. in 4½	,,	1½	,,

The specified heating-curve for silica bricks is intentionally slowed down over the range 290° to 320°.

The changes in height of the piece are plotted against temperature and time successively, as already indicated. A cylindrical furnace 18 in. in diameter, fired tangentially by gas or oil burners, is recommended. Similar pyrometers to those already mentioned are recommended, the cold junctions being maintained at the temperature of melting ice. A

[1] Anon., *J. Amer. Ceram. Soc.*, 1928, **11**, 462, 505.

furnace is described which takes duplicate bricks side by side, with a completely duplicated loading and indicating mechanism. Further details may be found in the original specifications.

Another design of Load-Test furnace in use on the Continent and also in England is that designed by K. Endell.[1] The notable features here are the use of a cylindrical test-piece 5 cm. in diameter and height, and that temperatures are observed on the top face of the test-piece by way of a central tube through the thrust-rod. This necessarily leads to lower temperature-readings than are obtained on the outside of the test-piece. Whilst the conditions are somewhat better from the pyrometric view-point, this difference should be clearly stated in reporting results which are likely to be confronted with those from other apparatus.

IV.—FIRED CLAYS AND CLAYWARES: GENERAL EXAMINATION

A. Porosity and Related Properties

All material must be thoroughly dry before testing. Porosity is defined as the proportion of empty or air-filled spaces; it is usually expressed as a percentage of the overall volume. A broad distinction is drawn between pores which communicate with the surface, and are readily filled by absorbed liquid (open pores), and those which are sealed up; pores which are closed, with the exception of a fine crevice, form an intermediate type, and may or may not be filled during attempted saturation with liquid. When methods calculated to fill all but sealed pores are used, the resulting porosity is known as "apparent porosity" and its dry weight divided by the volume of the apparently solid portion as "apparent specific gravity." The "true porosity" or porosity proper is derived from the true specific gravity (see p. 35) and overall volume (see below). The difference between "true" and "apparent" porosities is the proportion of sealed pores. A slight bulk expansion is characteristic of the adsorption of water into materials of fine texture, but this has so far been ignored in these measurements. "Absorption" is a term applied to more or less rough tests in the sense of the quantity of a liquid (usually water) absorbed, expressed as a percentage of the dry weight; the term is also used relatively in connection with the depth of penetration of a coloured liquid into porous materials. In fine earthenware manufacture a solution of a dye, such as fuchsin, malachite green, or red ink is commonly used as a test for the relative porosity of samples of biscuit ware and for the detection of crazing, pinholes, or other discontinuities in the glazed

[1] K. Endell and W. Steger, *Metall. u. Erz*, 1923, 20, 321.

surface of finished ware. The solution is poured over the piece, which is afterwards broken open, or, if glazed, the surface is cleaned in order to detect the penetration.

The British Porosity Test for Electrical Porcelain[1] specifies that broken pieces shall be selected, free from any external glaze, and immersed for twenty-four hours in a 0·5 per cent. alcoholic solution of fuchsin under a pressure of 2000 lb. per sq. in. (140 kg. per sq. cm.) without showing any signs of impregnation. The American method[2] is to use a strong iron container such as that shown in Fig. 24. A piece of ware is inserted. The vessel is completely filled with coloured alcohol, sealed, and alcohol pumped in up to a required pressure of, say, 50 lb. per sq. in. and held for fifteen minutes. The gauge should read to at least 80 lb. The piece is finally taken out, and the depth of penetration of colour measured. This measurement is recommended in preference to a record of the volume of liquid absorbed.

Porosity by Saturation and Volume Measurement

For water absorption and apparent porosity the dry, fired pieces (p. 80) are weighed, placed in distilled water and boiled for two hours; they are then left to cool in the water to as near 20° as possible (or cooled under running tap water), dried lightly with a *damp towel* to remove excess water and weighed to 0·1 g. The volumes of the saturated pieces are then determined in a suitable volumeter. A convenient method of obtaining the overall volume of saturated pieces or pieces coated with a known weight of paraffin wax, plasticene, etc., is to use the volumeter of W. Michaelis.[3] Many variations on this design have appeared from time to time. The apparatus consists of a wide glass vessel to receive the test-piece, with a cover which clamps on. A graduated glass tube rises from the centre of the cover. Delivery pipettes of 200, 100, 50 and 20 c.c. are provided. The capacity of the apparatus to a given mark on the graduated tube is known. The volume of the test-piece follows from that of the volume of water required, with the piece inside the vessel, to fill up to the given mark. The apparent porosity is obtained by dividing the volume of water absorbed by the total volume of the piece, expressing the result as a percentage. For apparent specific gravity the volume of water absorbed is subtracted from the total volume of the piece, thus giving the apparent solid volume, which is divided into the dry weight of the piece. The following method may alternatively be used.

[1] Anon., *B.E.S.A. Spec.*, No. 137, 1922, p. 9.
[2] Anon., *J. Amer. Ceram. Soc.*, 1928, 11, 496.
[3] Cf. *Deuts. Töpf. u. Zeigl. Ztg.*, 1879, No. 13.

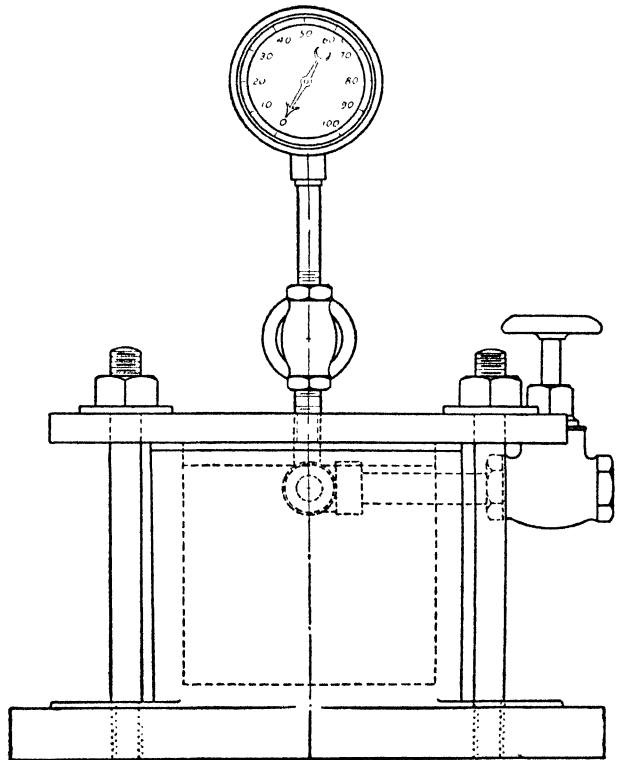
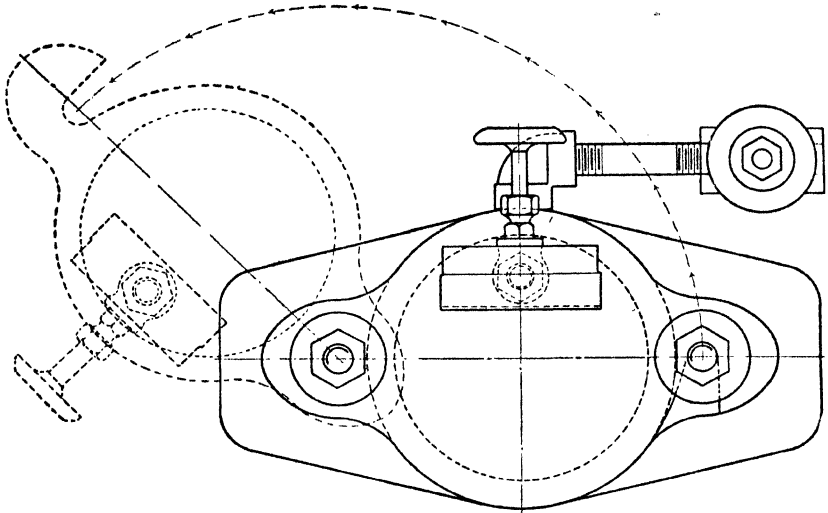



Fig. 24.

Porosity by Liquid Absorption and Weighing Immersed

For silica bricks it is recommended[1] to cut representative pieces into rough cubes of about 2 in. side. These are dried at 110° for about two hours, cooled in a desiccator and weighed (w_d). The pieces are then soaked in water for some hours, preferably overnight, under reduced pressure. A vacuum desiccator is convenient. They are then taken out and wiped free from surface water and weighed (w_s); the weight suspended in water (w_w) is then obtained, the piece being suspended by a fine thread of cotton or a very fine copper or rare-metal wire. Allowance is made for the weight of the thread. ($w_s - w_w$) is the weight of liquid which has a volume equal to that of the saturated piece. The porosity is given by the expression

$$P = \frac{w_s - w_d}{w_s - w_w} \times 100$$

Duplicates should agree within 0·2 per cent. It is assumed that, for this class of ware, all the pores are "open" pores, but with very dense, or close-textured materials, further precaution is necessary, such as soaking for two to three days, preferably under reduced pressure and with oil of turpentine, kerosene, xylene, paraffin or melted vaseline in place of water. Where such alternative liquid is used, its specific gravity (ρ) at the temperature employed is accurately determined, and allowance made in calculating the specific gravities. Using the above terms the sample has the following related characteristics—

$$\text{Bulk specific gravity} = \frac{w_d . \rho}{w_s - w_w}\text{; Apparent specific gravity} = \frac{w_d . \rho}{w_d - w_w}$$

An American method,[2] suitable for electrical porcelain, is as follows. A single specimen is taken, with at least 50 per cent. of its surface freshly fractured and weighing 30 to 50 g. It is dried at 120° (248° F.) ± 5° C. for twenty-four hours, cooled in a desiccator and weighed. It is then totally submerged in distilled water at about 20° and left for a hundred hours. The water is boiled for approximately one hour during the 1st, 25th, 49th and 73rd hours. After a hundred hours, the specimen is carefully dried superficially with a clean dry cloth and weighed. The original and subsequent weighings are recorded and the moisture content after soaking calculated as a percentage. The results from several specimens may be averaged.

Volume-Change on Firing. The overall volume determined by any of the methods mentioned may be used for correlation with the dry unfired volume; the change in volume is expressed as a percentage of the dry unfired volume.

[1] J. W. Mellor, *Trans. Ceram. Soc.*, 1918, 17, 314.
[2] Anon., *J. Amer. Ceram. Soc.*, 1928, 11, 476.

Apparent Porosity by Extraction of Air

(a) *The M'Leod Gauge Method.* An apparatus suitable for the determination of the very small porosity of such wares as electrical porcelain was devised by E. W. Washburn and E. N. Bunting. This all-glass apparatus is shown on the left of Fig. 25; on the right is the more robust modification due to L. Navias,[1] in which the glass capillary is welded directly on to a cap of 20 per cent. chrome steel.

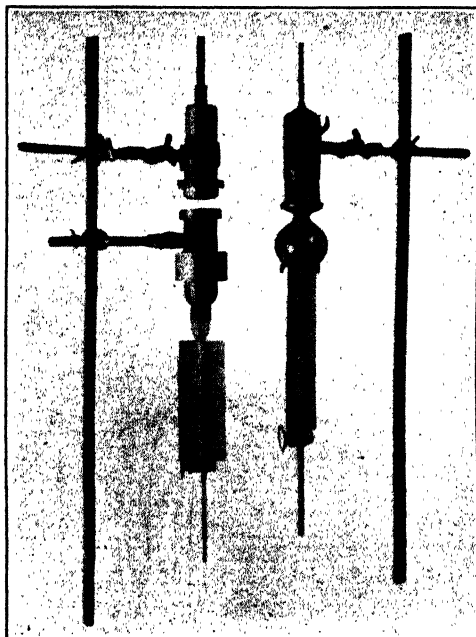



Fig. 25.

It is as sensitive as the all-glass apparatus. All dimensions are shown in Fig. 26. The cap fits on to the lower cup, designed to hold the test-piece (fractured pieces are best) and also to admit mercury from below. The joint may be simply secured by a rubber band under tension or in addition ground in and sealed with a thin layer of grease. A mercury reservoir and stout rubber tubing are connected to the base of the cup. A stop inside the vessel prevents the piece rising into the upper half when the mercury is admitted. The object of the test is to eject all air other than that in the pores of the piece and then expand the pore air by producing a vacuum around the test-pieces, by lowering the mercury reservoir to a marked level, 76 cm. below the base of the lower cup. A slight

[1] *J. Amer. Ceram. Soc.*, 1925, 8, 816.

entrapment of air occurs, which necessitates a previous calibration. This is permanently marked on the scale attached to the capillary, and becomes the zero of that scale.

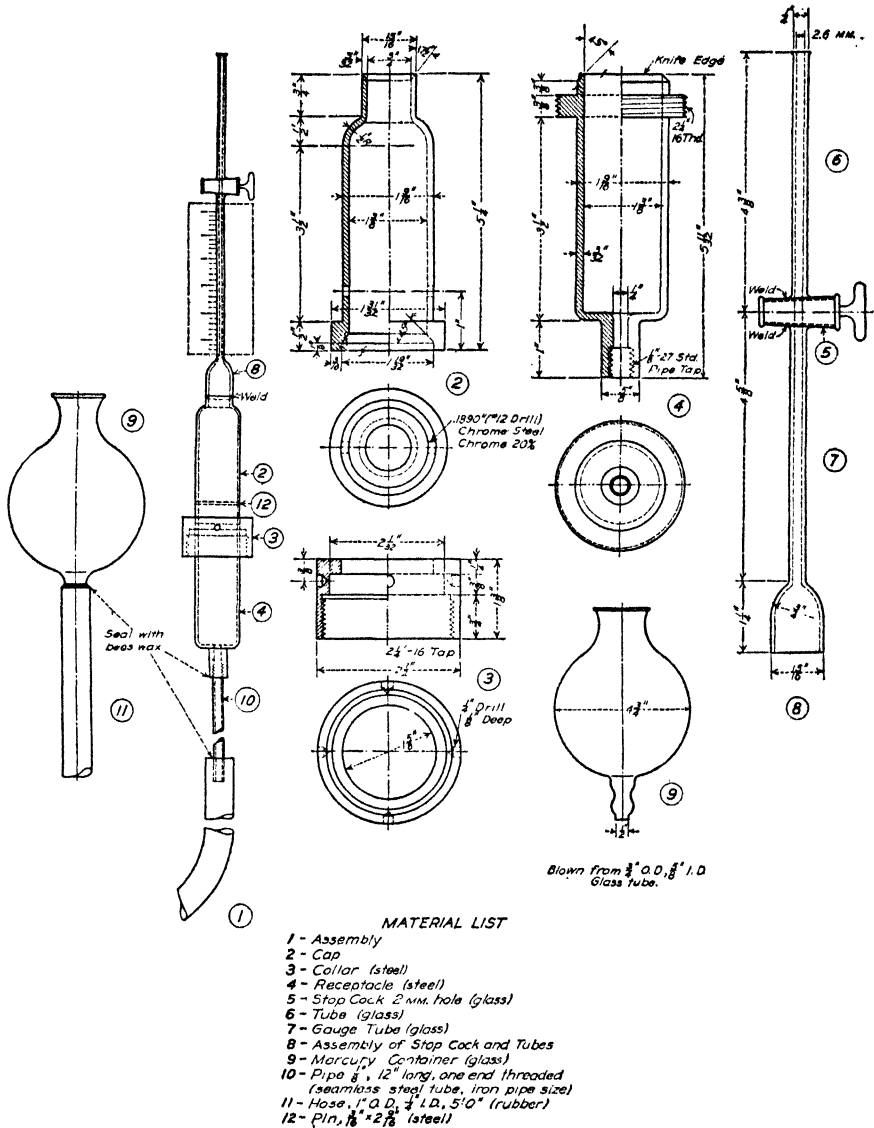



Fig. 26.

Pure, dry mercury and dry test-pieces must be used. In carrying out a measurement, the fractured specimens are sealed up in the apparatus, with the stopcock above the capillary open. The mercury level is raised to the cock and the latter turned off. The reservoir is then

fully lowered, thus expanding the air in the pores. The mercury level is then raised until the level in the reservoir and the capillary is the same. The reading is taken, the measured air ejected and the apparatus again flooded with air. The whole process is repeated a second and third time and the average of these latter volumes is taken as the pore volume present. This is expressed as a percentage of the total volume of the pieces, as obtained with any suitable volumeter.

This method yields notably higher results than saturation by four hours' boiling in water or the 100-hour test (p. 96), with samples having porosities in the range 0·25 to 0·75 per cent. This indicates that the penetration of water into very fine pores is unreliable.

(b) *M'Gee's Method.*[1] The apparatus is shown in Fig. 27. The air contained in the pores of the specimen is evacuated in successive stages and collected between the stopcocks *a* and *b* in vessel *C*. The capacity of *C* may conveniently be about 3·5 c.c. for porosities of not more than 3 per cent. or 1 c.c. for porosities up to 0·5 per cent. With a specimen 1 × 1 × 2 in., porosities up to 10 per cent. may be measured with the larger vessel. The test-piece may conveniently be 4 × 1 × 1 in., a form suitable for further tests such as transverse strength. It is contained in a jointed cylindrical vessel *D* about 5 in. long by 1½ in. diameter and of about 150 c.c. capacity, provided with a levelling-mark at *g*, and connected to a flexible metal-cased rubber tube *e* and a mercury reservoir *F*. The reservoir is graduated from an upper mark downwards in tenths of a c.c. to a total of 125 c.c.

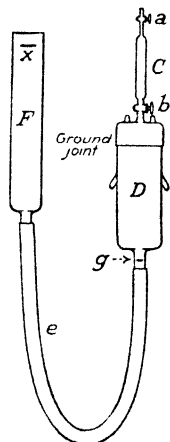



FIG. 27.

The volume of *D* is determined (from *g* to *b*) by filling with mercury from *F*, and the volume of the specimen subsequently inserted in *D* is determined by repeating the operation and noting the reduction in capacity of *D*. In detail, the mercury is set to the level *g*, and *F* filled up so that mercury stands at the zero *x*; *b* and *a* are opened and *F* raised until the mercury stands at *b*, where the reading on *F* is the volume between *g* and *b*. *F* is then lowered and the piece inserted in *D* and the ground-in top secured with rubber bands. The burette is then raised until the mercury again stands at *b*, *b* and *a* both remaining open. The new reading gives the volume of *D less* that of the specimen. The whole apparatus up to *a* is now cleared of air by raising the mercury level to *a* and closing the tap. Lowering the mercury to about *g* now releases part of the air in the piece and this is transferred to *C* by raising the burette sufficiently, *b* is closed and the mercury level

[1] *J. Amer. Ceram. Soc.*, 1926, 9, 814; Anon., *ibid.*, 1928, 11, 499.

again lowered as before and raised so as to collect a further portion of air in *C*. These two operations are recommended but more may follow if thought desirable. Finally the mercury level is raised to *b*, *b* opened and the level of mercury in *b* and *F* equalised, when a final reading gives the volume of air in *C*. The total capacity of *C* is determined as a preliminary. The apparent porosity is obtained by dividing the volume of air by the total volume of the piece and expressing the result as a percentage. Correction for entrapped air in *D* is obtained from a preliminary experiment with a piece of glass about 4 in. × 1 in. × 1 in.

At least ten determinations are recommended. Values 20 per cent. above or below the mean are discarded and not less than six values should remain.

Apparent Porosity by Change in Air-Pressure

This is an indirect method depending on the fact that a given change of volume of the air in a vessel containing a porous specimen produces a less change in pressure than would be the case with a non-porous specimen. M'Gee[1] describes an apparatus, convenient for use with specimens 4 in. × 1 in. × 1 in., which operates at reduced pressures of about $\frac{3}{4}$ atmosphere. This apparatus is suitable for porosities of over 10 per cent. It is necessary to note the barometric pressure p, at the time of the experiment. The apparatus is shown in Fig. 28.

A vessel, *A*, 5 in. long and $1\frac{1}{2}$ in. diameter and capacity about 145 c.c., having a ground-in joint, upper stopcock and lower mark, *K*, contains the specimen. The joint is secured in the usual manner. An expansion vessel, *B*, is attached to the base of *A*, and provided with a lower mark, *L*. The volume between *K* and *L* is accurately measured and may be about 50 c.c., though this volume may be increased to give greater accuracy. The tube from *L* downwards forms a *U* with a scale *D*; the second limb of the *U* is reduced to capillary diameter above the level of *K*. This capillary is so placed in order to avoid serious error in taking the volume of *A*, or, alternatively, the insertion of a second stopcock. The lower end of the U-tube is connected, through a rubber tube closely fitted in a flexible metal tube, with the reservoir and burette *C*. This has a capacity of 200 c.c. and is graduated downwards in tenths of a c.c. The accuracy of measurements is said to be but little affected by the usual accumulation of small amounts of dirt.

The volumes between *L* and *K* (= *B*), and *K* and the top stopcock (= *A*) are determined in a blank experiment. With the top cock open the piece is then secured in *A* and the apparatus filled with mercury to the level of *K* and the zero on *C*. The top cock is then closed and the

[1] Anon., *J. Amer. Ceram. Soc.*, 1928, 11, 501.

mercury level lowered to L, when the pressure difference, R, is read on D. The volume of the test-piece is then obtained by raising the mercury level, opening the cock and raising the mercury level to the stopcock. C is then read for the volume, v, of the piece. The total air space between K and the cock is $\frac{(p-R)\times B}{R} = a$; then the solid volume (s) of the piece is $A-a$; consequently the apparent porosity is

$$P_a = \frac{v-s}{v} . 100 \text{ per cent.}$$

Ten determinations are to be done and values 20 per cent. above or below the mean are discarded; not less than six values should remain,

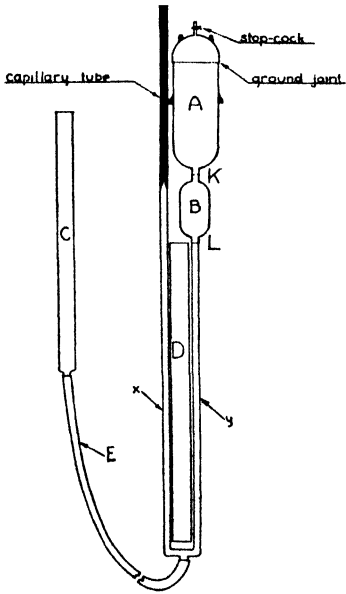
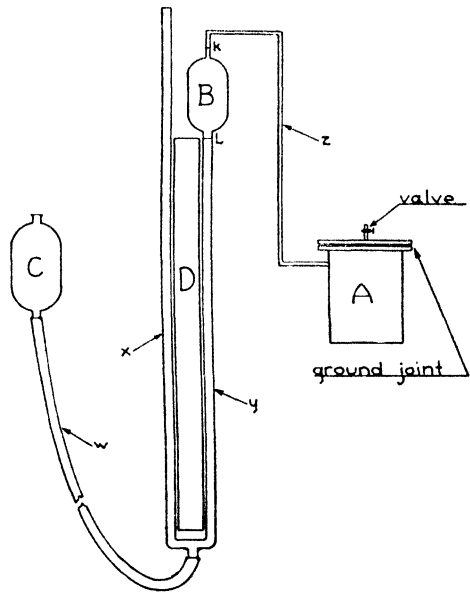



Fig. 28. Fig. 29.

otherwise a duplicate series should be carried out and similarly treated. The apparent specific gravity is given by dividing the dry weight by the displacement-volume, v.

Apparent Porosity by Change in Air-Pressure (Bricks)

This apparatus, Fig. 29, is adapted to direct porosity measurements on whole bricks. The superficial volume is calculated from the linear dimensions in cm. The brick container is but slightly larger than the specimen.

The apparatus is modified from that of Fig. 28, in which A is replaced by the larger container (about 2000 c.c.) and C becomes a simple mercury reservoir. B has a capacity of about 250 c.c., the

capillary diameter of the free limb of the manometer is no longer required and the manometer tubes have a diameter of about 5 mm. The container is joined to B by a capillary tube. The container has a cover plate with a soft rubber gasket and is clamped in place by eight wing-nuts. If desired the joint may be ground to fit and greased. Ordinary heavy-walled tubing may be used for the mercury reservoir, which may be of metal. B and D are of glass, but being permanently fixed, they are relatively secure from injury.

The procedure is to fill up with mercury to the mark K, place the piece in A and seal up; the valve on A is then closed. Lower the mercury level to L; read the pressure difference, R, on the scale. If the barometric pressure is p, the volume of the container up to K is A, the volume with piece in position, a, and the solid volume of the piece, s, then

$$a = \frac{(p - R)B}{R}; \quad S = A - a,$$

and

$$\text{Apparent Porosity} = \frac{v - s}{v} . 100,$$

v being directly measured.

The accuracy of the method is stated to be well within routine requirements. Ten determinations should be done and results deviating more than 20 per cent. from the average be rejected; if less than six results remain, the series should be repeated.

Permeability to Water (Roofing Tiles)

Samples of a size to absorb 20 to 25 c.c. of water are thoroughly dried and their edges coated with paraffin wax. A cylindrical glass tube of 10 sq. cm. end area is waxed to the upper surface of each. 10 c.c. of water is delivered into the tube and the time required for its absorption noted. A further 10 or 15 c.c. is added and the time noted when dew first appears on the under side of the tile. 10 c.c. more is added and the time required for the first drop to fall off the under side is noted, or the quantity or rate of flow through the specimen, with a definite head of water may be observed. For the best results, temperature should be controlled.

B. Strength: Resistance to Variously Applied Stresses

Tensile Strength

The method already described (p. 73) may be used for fired pieces; the experimenter must be prepared for the considerably higher strengths met with in fired ware. Tests on whole bricks may be carried out with the self-aligning grip described by J. W. M'Burney.[1]

[1] *J. Amer. Ceram. Soc.*, 1928, 11, 114.

A standard method has been proposed for electrical porcelain by the American Society for Testing Materials[1] and adopted by the 1928 Committee of the American Ceramic Society. This test may be adapted to a wide range of purposes. The aim of the special features of this test is to subject the sample to a truly axial load, applied in such a way as to minimise the chance of an abortive break-down.

Test-piece. Fig. 30 shows the form of the test-piece. It consists of two conical parts of basal diameter $1\frac{25}{32}$ in., having sides sloping at $7\frac{1}{2}^\circ$ to the axis, truncated at a length of $2\frac{1}{2}$ in. and a diameter of $1\frac{1}{8}$ in., the truncated ends being united by a cylindrical part 1 in. in length. The length of the whole piece is 6 in. in the fired state. The method of making depends on the process required, thus:

Wet-Process. Force the batch-mixture through a die; sections of the column, after thorough drying are turned to the desired shape and

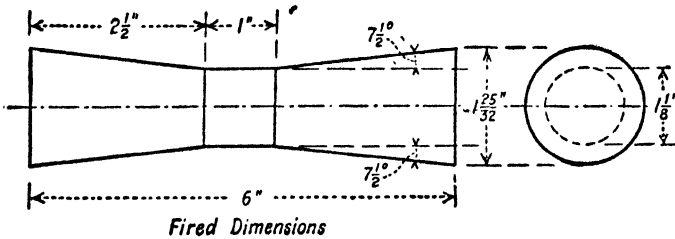



Fig. 30.

fired so as to maintain the axis perfectly straight. Due allowance for shrinkage must be made.

Casting. Specimens are slip-cast in plaster moulds of the desired final form, with allowance for all shrinkage. Only the fins may be removed and the pieces dried and fired so as to remain straight.

Dry-Process. The mixture in a proper state is formed by pressure in metal moulds of such dimensions as to give the correct fired size.

The Machine. Figs. 31 and 32 show a suitable machine and its parts. The conical ends of the test-piece seat into steel conical split-ring bushings, there being an intermediate gasket of blotting-paper or sheet lead $\frac{1}{32}$ in. thick. The gasket may be held by a temporary clamp, during fitting up, the clamp fitting on the piece over the zone of minimum section. The correct alignment of the specimen is assured by a gimbal mounting for each end grip. The split rings are held in rings which are conically shaped inside and attached to outer rings in the same plane by means of diametrically opposite pin bearings. These outer rings are attached by pins whose alignment is

[1] Ser. Desig. D 116-27 T; Anon., *J. Amer. Ceram. Soc.*, 1928, 11, 468.

in a vertical plane at right angles to the inner axis: the pins are attached to yokes above and below the piece. The upper one is connected to the machine. One of these yokes is fixed, while the load is applied to the other at such a rate that it can be accurately weighed. The error, in the loading range, should not exceed 1 per cent.

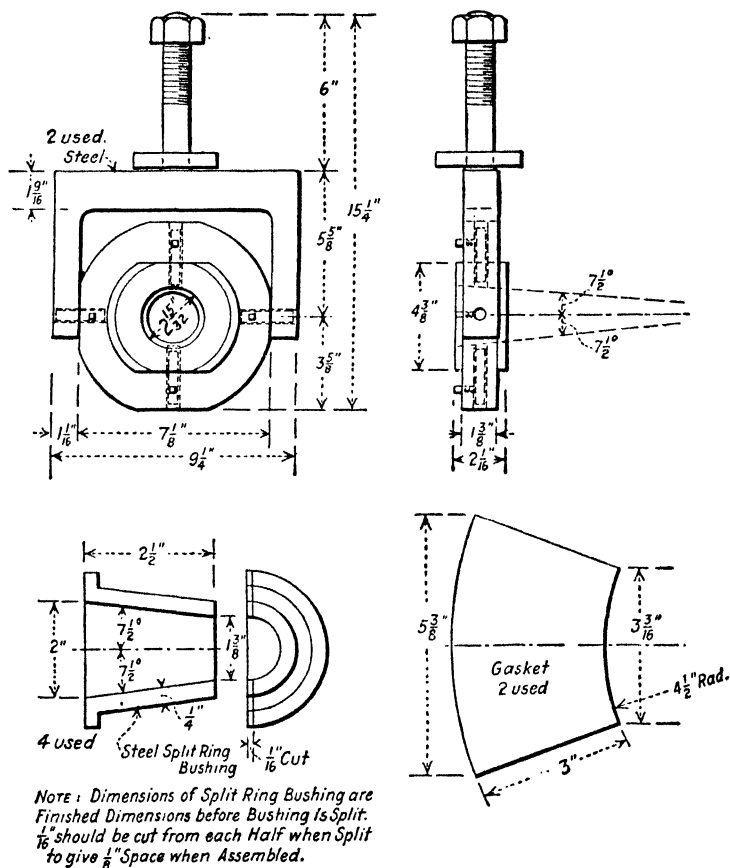



FIG. 81.

Not less than five specimens are tested in the normal condition. The average diameter at the zone of least cross-section is taken on two diameters at right-angles with a micrometer graduated to 0·001 in. (0·025 mm.). The temperature of testing should be about 21° (70° F.). Results on specimens not breaking at the minimum cross-section are to be included, the stress being calculated on the minimum section. Any result deviating more than three times the mean of the deviations is discarded. Normally, the whole area of fracture is very coarsely granular, the whole area being subject to tension and resisting it.

Where a flaw exists, the fracture tends to start near it, or pass through it; the surface near the flaw will be much smoother than the rest. If the specimen is compressed at the narrow portions, near one of the grips, an area of shear will radiate from the spot most under compression. It is consequently of importance, in reporting results, to note the nature of all fractures, rough and smooth parts, pin-holes and other flaws; also the behaviour during loading. In reporting

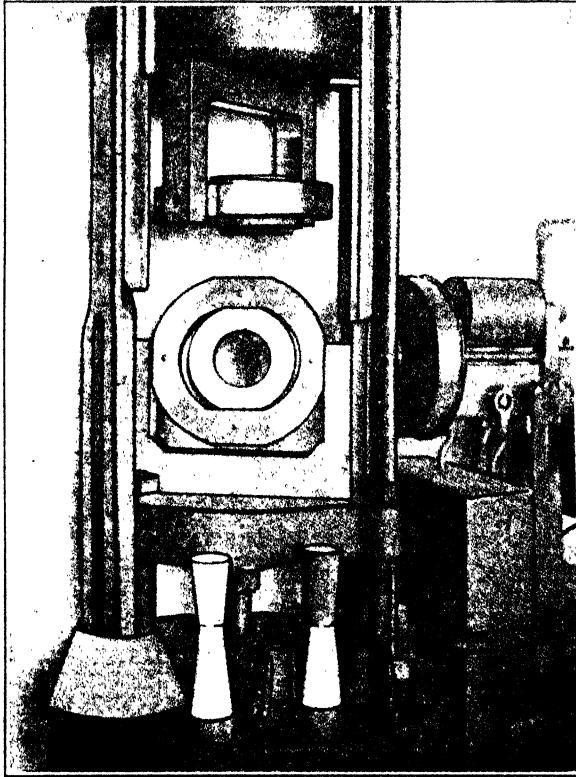



FIG. 82.—Apparatus for tension testing of porcelain, including grips, specimen split ring, and blotting-paper gasket.

results, note for each specimen the breaking-load (lb.), the diameter of the break and of the minimum section, remarks on fracture, etc., rate of application of load and name and rating of machine used. In addition, give the average of the tensile strengths and the percentage average deviation from the mean. The results may be plotted statistically by arranging the results in order of magnitude.

Tensile stresses are chiefly involved in the testing of pipes for bursting strength (see p. 112).

Transverse Strength and Elasticity by Transverse Loading

The general form of all the tests which come under this heading is the same, but the nature of the test is varied to suit the requirements imposed for different wares in respect of shape and dimensions of test-piece. In general the specimen is symmetrically mounted on two knife-edges and has a stirrup across it midway between these so that a load may be applied. Data for elasticity may be derived from the lower loadings and the transverse strength from the breaking load. The simplest equipment serves for most purposes where transverse strength only is required.

A. E. M'Gee[1] describes a somewhat more elaborate apparatus having a wide range of usefulness. Figs. 33 and 34 show the main dimensions and also the general lay-out. The block which supports the test-piece on a 3 in., 5 in., or 7 in. span is firmly fixed to a table top. The load is applied medially on a stirrup which is connected below the test-piece to a rod which passes through the centre of the supporting block to a lever suspended below the table top. This lever is counterbalanced at one end and loaded at the other. Arrangements may be made for lever ratios of 5, 7 or 14 to 1, thus facilitating tests on a wide variety of materials from green bodies to hard-fired specimens, such as porcelain. A container holding lead shot is fixed to the table top and feeds the loading-bucket through a hole. When rupture of the test-piece occurs the lever drags a shutter across the hole and thus automatically arrests the flow of shot. The exact distance between the knife-edges is carefully measured, together with the breadth and depth of the piece; these latter are required to be measured to the nearest $\frac{1}{64}$ in. For elasticity measurements, the deflection of the centre of the bar, and, preferably, above the lower knife-edges also, is measured in $\frac{1}{10000}$ in. by means of Ames dials. An initial load of 21 lb. on the central knife-edge is recommended. Thereafter the load is increased intermittently and the deflections noted. The loading is carried up to about three-quarters of the breaking load. The deflection is taken as that of the central indicator, *less* the average of the deflections of the two end indicators. The changes in deflection are correlated with the changes in load and the elasticity calculated according to the expression:—

$$E = \frac{ml^3}{4Sbd^3}$$

where E = Young's modulus of elasticity; m = the load range corresponding to the deflection (S), in lb.; S = deflection of the centre of the piece, in inches; b = breadth and d the depth of the piece, in inches; l = distance between lower knife-edges, in inches.

[1] *J. Amer. Ceram. Soc.*, 1927, 10, 569; Anon., *ibid.*, 1928, 11, 514.

Shot Container Box
Hole
⅛"x1x5' Iron Bar
Gallon Bucket for Receiving Shot
Table Leg
Table Top
U-Bolt for Bar Check
2"x½"x55" Iron Bar
35"
⅛"x1"x2½" U-Bar
1½"x2"x8" Iron Bar
Rods for Supporting Dials
Ames Dials
1"x1"x6' Test Piece
Bolts for Fastening to Table Top
½" Iron Rod
Two 5"x¼"x5" Iron L's for Supporting Bar from Table Top
⅛"x1"x5" U-Bar
5"
Bucket for Holding Counter-Weight Shot
Shot Container Box
Hole for Shot to Pass Through
⅛"x1"x5" Iron Bar that Moves Back and Forth So that Hole Comes In and Out of Line Thus Starting and Stopping Flow of Shot
U-Bolt for Bar Check
U-Bolt for String to Run Through
Cord Tied to Lever Bar
Lever Bar
Table Leg
DIAGRAMATIC SKETCH OF MACHINE FOR DETERMINING ELASTICITY AND TRANSVERSE STRENGTH

Fig. 33.

Ten determinations should be made, and values deviating more than 20 per cent. from the mean should be discarded, leaving not less than six good values. Otherwise the series should be repeated.

It is apparently intended that the total deflection should be utilised over as wide a range as is consistent with proportionality between load and deflection and that ten separate pieces be tested. For some purposes it may be useful to calculate the modulus for each loading and plot this graphically against the total load.

For a simple determination of modulus of rupture with the above apparatus the indicating dials are not required. The load should be

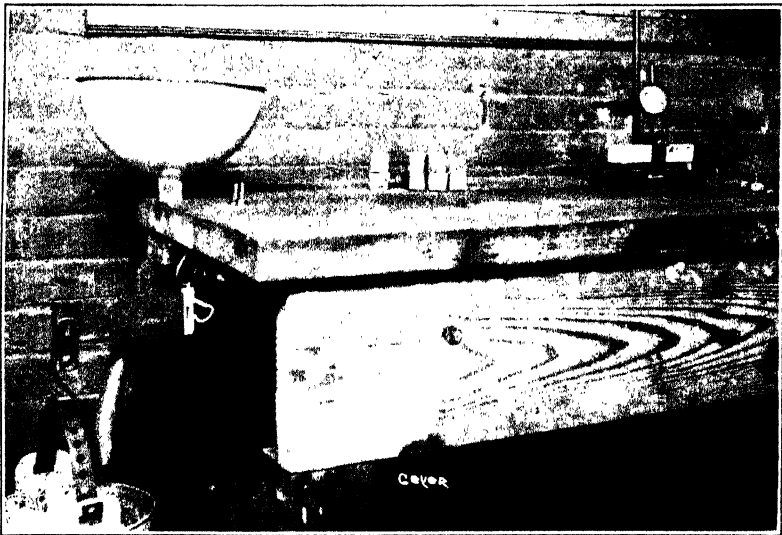



FIG. 34.

applied at a rate of about 60 lb. per minute until rupture occurs. The shot-bucket and its contents are then weighed on a small double-beam platform scale calibrated to ¼ oz. The modulus of rupture (M) is given by the formula $M = \frac{3}{2} \cdot \frac{Pl}{bd^2}$, where P is the breaking load in lb. and the remaining symbols have the same meaning as given above.

With less accuracy, both moduli may be determined together using but one Ames dial. An initial load of 21 lb. is imposed and the dial reading noted. The loading is then carried out as for rupture and the reading for deflection taken as nearly as possible before rupture occurs. The load-range for the calculation of elasticity is, of course, the total breaking load less 21 lb. An accuracy of 0·25 per cent. is stated to be practicable.

Transverse Strength with the Riehle Testing Machine.

This method is adapted to the Standard Riehle tensile strength machine.[1] The necessary attachment is shown in Fig. 35. It consists of a supporting bar suspended by the ends. This bar is notched at 3-in. and 5-in. spans so that a piece supported on round rods

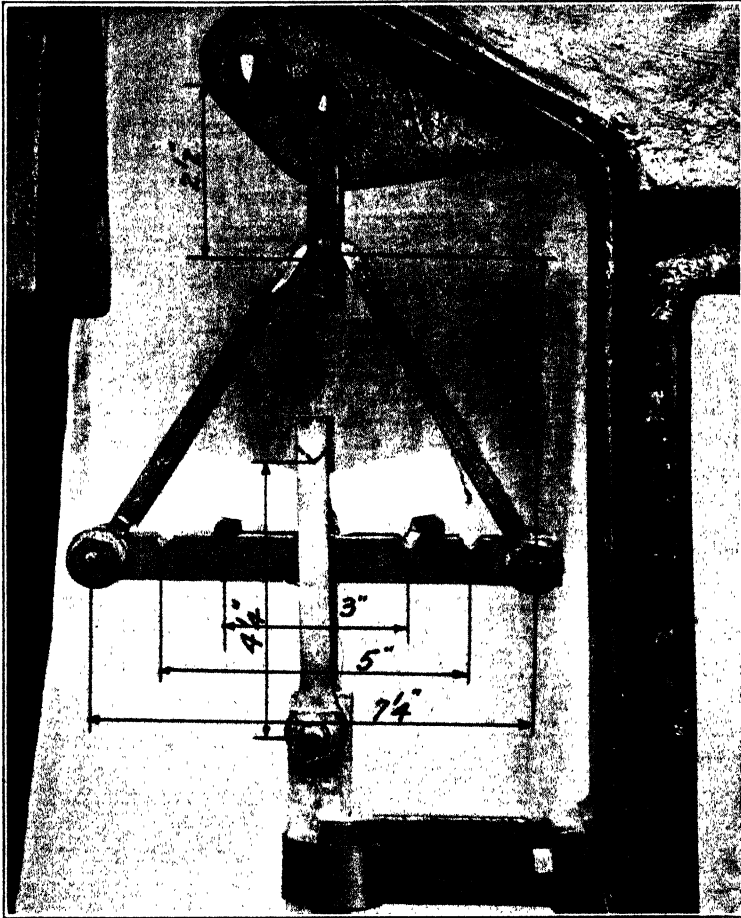



Fig. 35.

in these notches may be broken at the desired span. The stirrup, with a knife-edge resting on the centre of the piece, is attached below. The test-piece is 1 in. square and of a suitable length. "The upper bearing or knife-edge is lowered by means of the hand-screw wheel to make contact with the centre of the test specimen. (Badly warped test-pieces prevent equal distribution of load and should be discarded.)

[1] Anon., *J. Amer. Ceram. Soc.*, 1928, 11, 513.

The lever arm of the machine is drawn to a horizontal position by means of the hand crank connected with the hand screw and must be maintained level throughout the test by turning this hand crank. The load is applied by releasing the shot contained in the receptacle at the other end of the lever arm. When the test-piece breaks, the flow of shot automatically ceases, and the breaking load is indicated by the weight of shot which has flowed out into the scale pan."

The modulus is calculated in the manner explained above. Ten specimens may be taken, and 60 per cent. of these should deviate less from the average than 20 per cent. of this figure. The accuracy obtained depends on the structure of the piece and its contacts with the bearings.

Transverse Strength of Electrical Porcelain

The following method and dimensions are recommended[1] for electrical porcelain test-pieces prepared under the conditions mentioned above for tensile test-pieces of this material. The test-pieces are cylinders 6 in. (15·2 cm.) long and 1·125 in. (2·86 cm.) diameter, supported on steel wedge-shaped blocks with edges rounded to 0·125 in. (3·175 mm.) radius. These blocks, or "knife-edges," are placed 5 in. (127 mm.) apart, and the specimen is allowed a half-inch (12·7 mm.) overlap at each end. An apparatus such as that shown in Fig. 35 may be used. The load is applied centrally on top of the test-piece and at right angles to it by means of a wedge-shaped pressure piece whose angle is 45°. The actual edge is rounded off to 0·125 in. radius. Measurements of the diameter of the test-piece are to be taken at right angles to the axis and at the mid-section. The load is applied at a constant rate, keeping the beam well balanced. The results are calculated from the formula—

$$M = \frac{8PL}{\pi d^3},$$ where P = load in lb. at rupture,
L = distance between supports, in.,
d = mean diameter, in.

The report is to be given in similar form to that for the tensile strength of electrical porcelain (p. 103), including the diameter and length of each piece and its modulus of rupture.

Transverse Strength of Whole Bricks

The modulus of rupture of whole bricks is required for some purposes; its determination is described as the Flexure Test.[2] Any

[1] Anon., *J. Amer. Ceram. Soc.*, 1928, 11, 472. [2] Anon., *ibid.*, 1928, 11, 479.

form of standard testing machine, with suitable knife-edges such as those shown in Fig. 36 can be used. A properly calibrated portable apparatus may be employed.

It is recommended (*loc. cit.*) that five whole bricks be successively tested, lying flat on a 7-in. span, with a load applied at the mid-section of the span. The knife-edges are of cast-iron in the form of an equilateral tetrahedron of 4 in. side. This is set so that the top edge acts as a knife-edge for the specimen, whilst the bottom edge, lying at right angles to the knife-edge and in a plane parallel to the length of the specimen, allows of free sideways adjustment to the specimen. Lengthwise adjustment is also secured by rounding the bottom edge

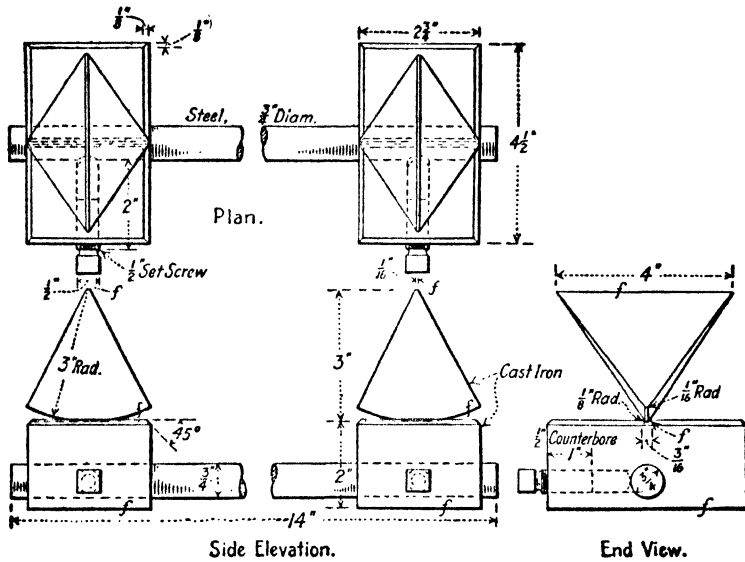



FIG. 36.

to a 3-in. radius centred on the mid-point of the knife-edge. The upper edge is slightly flattened. These features are shown in the illustration, but other types of knife-edge, ensuring free movement and full and even bearing, may be used. On the top of the specimen, at the mid-section, is placed a ½-in. square rod long enough to span the specimen and on this bears the upper knife-edge to which the load is applied. Both the rod and the knife-edge are placed midway between, and parallel to, the knife-edges.

In conducting the test the speed of travel of the head of the machine should not exceed 0·05 in. per minute. The modulus is calculated from the formula $M = \frac{3Pl}{2ba^2}$, in English units. The meaning of the symbols is given above (p. 110).

Transverse Strength of Tiles, etc.

A German method[1] is to provide the lower side of the tile with two parallel strips of portland cement, each 1 cm. wide and having 20 cm. between. The upper face is provided with a single parallel strip equidistant from the lower pair. The tile is then supported on the lower strips and loaded on the upper.

Bursting Strength of Pipes

The pipe is secured between suitable end-pieces, one of which is bored and fitted with a pressure-pipe. The assembly is then tested to a specified limit, or to destruction, under hydraulic pressure.

Rudeloff's method[2] specifies the use of leather covers for the pipe ends, made tight by coating with gelatin. Cylinders of iron or wood are secured to these covers, and one is bored for the pressure pipe. To give a firm grip for the leather covers, the pipe is placed between two cross-bars, and these pressed against the cylinders by a coupling rod, so that they do not come in contact with the ends of the pipe itself. A special machine for this test is now supplied by the Rawdon Foundry Co., Moira, Leics.

Compression Tests

These tests are chiefly used as a check on the load-bearing capacity of structural materials, particularly in the form of bricks. The test of Refractoriness-under-Load (p. 89) is a variant in which the effects of high temperature and load are combined in testing furnace building materials. Compression tests are also used as a measure of strength for all types of ceramic goods, bodies, etc.

Compression Tests on Fine Ceramic Bodies

For small, specially made trials, such as are convenient in testing fine ceramic products the following details[3] may be used as a standard (see also below). The test-pieces are cylinders $1\frac{1}{8}$ in. (2·86 cm.) in diameter and in height. The flat surfaces are made as smooth and parallel as possible before firing and, after firing, are ground smooth and parallel. In testing, a fresh contact-pad, or cushion, of blotting-paper $\frac{1}{64}$ in. thick is used on each face. The loads at initial and final failure are to be noted (in lb.) and the latter used for calculating the strength in lb. per square inch.

A. Jourdain[4] describes a modification designed to make the test more sensitive. He applies it to samples of "refractory products," but the method appears to be of general significance. Test-pieces cut to cubes of 5 cm. side are crushed in a suitable machine with a disc of

[1] Protokol, 20th September, 1890, *cf. Deut. Töpf. Zeigl. Zeit.*, 1893, 34.
[2] *Mitteil Königl. Versuchsanstalt*, 1892, 101.
[3] Anon., *J. Amer. Ceram. Soc.*, 1928, 11, 471.
[4] *La Cér.*, 1928, 31, 230.

rubber of about ½ cm. thick on either side. A sharp fracture is obtained and the pieces are claimed to break usually within 5 or 6 per cent. of the average.

The actual size of the test-piece has an undefined but often considerable effect on the result, which, combined with considerations of convenience, has led to varying sizes of test-piece being adopted with different materials. Thus, the recommendations of the American Ceramic Society in 1928 [1] also include the following:—*Grinding wheels:* a wheel 3 in. diameter and 2 in. thick. *Heavy clays, fireclays, etc.:* a cube of 3 in. side. *Whiteware bodies and allied materials:* a cube of 2 in. side. In addition to these, tests are frequently conducted on commercial sizes of firebricks, drain pipes, grinding wheels, wall-tiles and other goods.

Various types of press are available. Hydraulic presses are very convenient. An Olsen machine recommended by the American Ceramic Society (*loc. cit.*) consists of very hard steel pressure plates, a hand-screw for adjusting the height of the upper plate, hydraulic pressure applied to the lower plate, on the principle of the Bramah press, and a motor to drive the pressure piston at a steady rate. The pressure is measured by balancing the force exerted on a piston in a small auxiliary cylinder. The load is taken up by levers in two stages and measured by the position of a sliding weight on a calibrated lever. The driving pulley is disengaged from the plunger screw as soon as the piece fails. The machine is capable of giving loads up to 200,000 lb., and at least 15,000 lb. pressure should be developed for good results. By the use of interchangeable lever riders, the degree of sensitivity is, however, variable over a considerable range.

In using the above machine it is recommended to place three layers of cardboard between the specimen and the top and bottom plates of the machine. This is said to be satisfactory and much more convenient and cheaper than capping the specimen with cement or plaster, the use of lead plates, grinding the faces smooth and parallel, etc. The strength at final rupture is calculated in lb. per square inch. Ten determinations may be carried out, rejecting results 20 per cent. above or below the mean. Not less than six results should remain, from which the final average is derived.

Crushing-Strength of Bricks or Half-Bricks

In the specification of the American Society for Testing Materials,[2] a hemispherical bearing block as shown in Fig. 37 is recommended. The bearing surface is well oiled. The test-piece is a half-brick laid flat. Residues from the flexure test can be used, the ends being cut down, without damage to the remainder, until they are approximately flat

[1] Anon., *J. Amer. Ceram. Soc.*, 1928, **11**, 526.

[2] A.S.T.M., Ser. Design. C 69-27 T; *J. Amer. Ceram. Soc.*, 1928, **11**, 477.

and parallel. Five or more half-bricks should be cut from different bricks and prepared as follows. The two surfaces to take the load are given a thin coating of shellac and allowed to dry thoroughly. Any depressions of recessed or panelled bricks are filled with neat Portland cement mortar and left for at least twenty-four hours. One of the bearing surfaces is then coated with a thin layer of neat plaster of paris mortar and a good surface obtained by pressing on plate glass or a machined metal plate previously oiled or covered with waxed paper. The same preparation is accorded to the other surface, taking care that the two bearing surfaces are parallel.

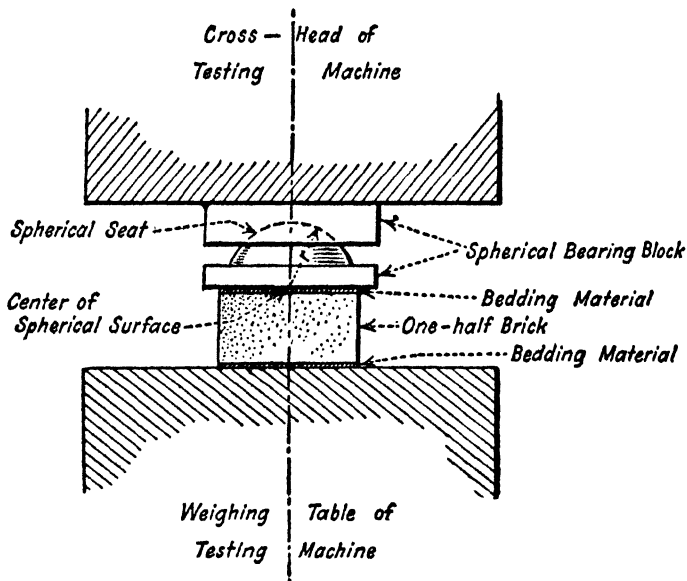



FIG. 37.

In testing, the piece is placed in the machine and the hemispherical bearing-block placed uniformly on top and adjusted under a small load. The load is then applied steadily at a rate not exceeding 0·05 in. per minute, whilst the beam of the machine is kept constantly floating. In calculating the strength, the total load sustained (lb.) is divided by the area (sq. in.) of the least plane (presumably excluding filled "frogs," etc.) at right angles to the direction in which the load was applied.

In the British method[1] of determining the cold crushing strength of refractory materials, at least five firebricks $9 \times 4\frac{1}{2} \times 3$ in., are taken and their normally horizontal faces ground parallel. The directions given do not bar the use of plaster of paris or thick cardboard for

[1] J. W. Mellor, *Trans. Ceram Soc.*, 1918, 17, 328.

taking up slight irregularities, in place of grinding, nor the use of any suitable form of machine. The machine there illustrated is shown in Fig. 38. This is Weber's machine, with the addition of power operated controls for driving a piston regularly in and out of a cylinder filled with castor oil. The lower patten of the press is integral with the piston, while the upper patten is adjustable by hand so that the brick may, initially, be lightly gripped. The pressure on the head of the piston (lb. per sq. in.) is registered on one of two dials of different range provided with maximum markers. Free pulleys, a worm gear and to and fro driving pulleys operate the primary pressure shaft. The whole machine is heavily made and bolted down

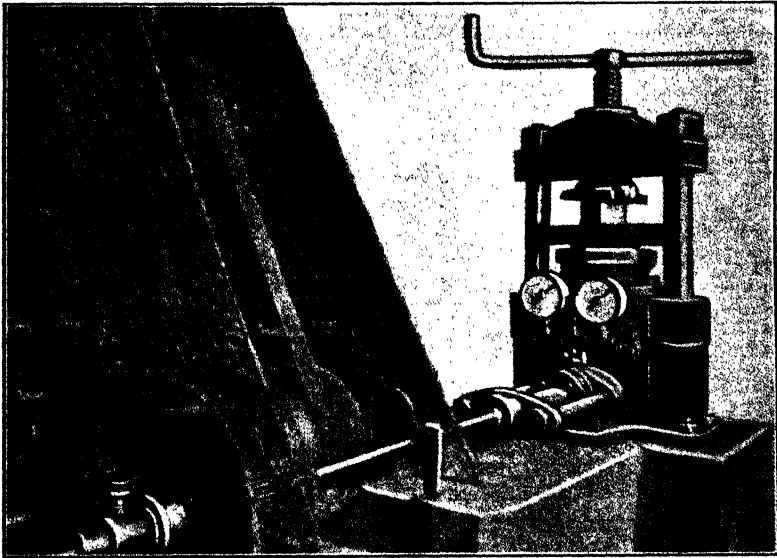



Fig. 38.

to a solid concrete bed. A valve and pump are provided for filling up with oil, and air below the piston is driven out by applying pressure on a block of iron. The normal rate of rise of the piston is 0·25 in. per minute. Before testing a brick, the piston is withdrawn fully, the lower patten of the press is levelled, the brick placed in position, and the upper plate adjusted so as to grip the specimen lightly. Pressure is then applied until collapse occurs. In calculating the result the gauge pressure (lb. per sq. in.) is multiplied by the area of the piston head (93 sq. in. in the machine at Stoke) and divided by the area of the brick (sq. in.).

In Germany it is customary to cut the brick through, reverse one half, and cement the pieces together so as to have half of the panel (frog) on each side.

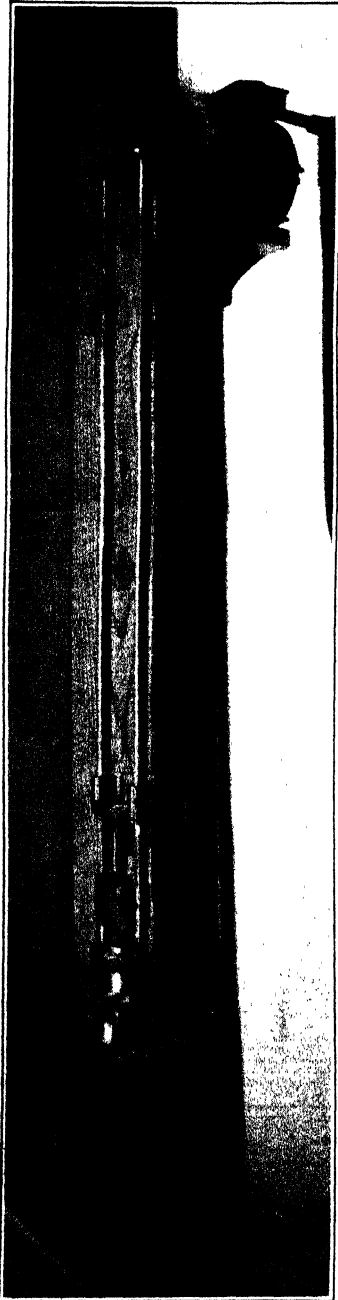



FIG. 39.

The choice of a suitable test-piece is still the subject of further inquiry.

Impact and Abrasion Tests

1. *The Olsen Impact Strength Machine*[1]

A weight falls between two guides and transmits its momentum to the test-piece through a short intermediate bar resting on the specimen. The latter is bedded on ten sheets of newspaper to distribute the load. The weight is raised automatically by a trigger attached to a cord actuated by a small motor (Fig. 39). A series of adjustable fingers attached to an adjacent vertical bar enable the trigger to be released at any desired height from which the weight is required to fall.

The machine may be used to cause failure of the specimen either by a series of equal blows, or by a series of blows of increasing severity. The number of blows, height of fall and mass of the falling body are recorded and the impact strength is calculated as the total momentum absorbed up to failure. Thus, for a series of equal blows the strength is expressed by $mn\sqrt{2gd}$ g. cm. per second, where m is the mass of the falling body (g.), g the acceleration due to gravity (980 cm. sec.$^{-2}$) and d the distance of fall of the weight (cm.).

Ten or more specimens of a convenient size are tested and the whole series rejected if over 40 per cent. are outside the usual 20 per cent. limits based on the average. As the factor of fatigue is not taken into account in these tests, it is recognised that the strength of specimens rises in a greater ratio than the calculated figure.

Another form of the test[2] employs a hammer with a hemispherical striking face. The hammer is hinged at the handle and mechanical arrangements

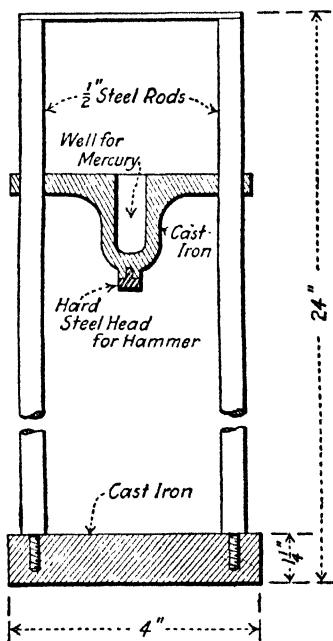
[1] Anon., *J. Amer. Ceram. Soc.*, 1928, **11**, 521. [2] *Ibid.*, p. 524.

may be made for continuous tapping until failure occurs. The number of blows given is shown on a revolution counter.

For electrical porcelain testing the following method is recommended.[1] The apparatus is shown in Fig. 40. The apparatus consists of a cast-iron plate with clamps to hold in an upright position a cylindrical test-piece 1⅛ in. in height and in diameter. Two ½-in. steel rods act as side supports and guides for a mass of 1 lb., and are provided with stops at every ½ in. of height above the top of the specimen. The hammer is in the form of a cast-iron well for mercury with a hard steel head below, and side pieces running on the uprights. The apparatus may be operated by hand or driven by a small motor with arrangements for automatically increasing the height of the hammer. In testing a specimen the hammer is allowed to fall on the specimen from a height of ½ in., then 1 in., 1½ in. and so on until the specimen fails by cracking or breaking. The specimens may be made by any of the methods described above (p. 103) for electrical porcelain. Not less than five specimens are tested and the results averaged. The report should include, for each specimen, the number of blows tolerated, the energy of each in in.-lb. and the total energy for all the blows in the same units.

FIG. 40.

2. *The Charpy Pendulum*

The instrument described by L. Navias[2] is made by the Bell Telephone Co., and shown by Fig. 41. The specimen is gripped firmly at each end in variable supports on the heavy base-plate and attached to the framework which supports the pendulum. This frame resembles a gallows of channelled sections, approximately one and a half times the length of the pendulum. The latter is supported in ball bearings and attached to the framework at about two-thirds of its height. The axis of the pendulum is so placed that the test-piece is struck a horizontal blow midway between the posts of the gallows. The pendulum has an effective weight at the centre of the striking edge of exactly 1 lb.; the radius on which this point moves is 13 in. and the weight descends exactly 2 ft. before hitting the specimen. Apart,

[1] Anon., *J. Amer. Ceram. Soc.*, 1928, **11**, 473.
[2] *J. Amer. Ceram. Soc.*, 1927, **10**, 90; *ibid.*, 1928, **11**, 509.

therefore, from frictional corrections, the energy of the striker at the moment of impact is 2 ft.-lb. and the residual energy, after breaking the piece, is equal to 2 ft.-lb. multiplied by the numerical fraction of 2 ft. to which the bob subsequently ascends. This height is indicated by a semicircular scale attached to the gallows.

The pendulum moves behind the scale, whilst, rigidly attached and parallel to it, is a small arm in front of the scale. This arm moves a pointer. It is provided with a spring which enables the pointer to rest in any position on the scale at which it may be placed. It thus acts as a maximum indicator. The scale is made from a working drawing of a semicircle of 13 in. diameter (giving the path of the impact edge). Horizontal parallel lines $\frac{1}{100}$ ft. apart are drawn, and the intersections of these with the curve are connected to the centre and marked out on a concentric scale of 6 in. radius. Each division on this scale therefore represents 0·01 ft.-lb.; naturally they are more crowded towards the centre of the scale. These are the theoretical values and are subject to the corrections given on the concentric scales. The pendulum absorbed, in a particular case, 0·035 ft.-lb. for an entire swing of about 296°; half of the *frictional* energy had been absorbed at the point of impact. The amount of the friction is given as proportional to the linear drop of the pendulum and is equivalently proportioned between 0·0175 and 0·035 ft.-lb. To this is added the friction of the indicator, which depends on an angular relationship and is found, in the given case, by dividing up the angular scale into equal increments proportional to a loss of 0·020 ft.-lb. for a movement of 148° starting from the angle of impact. Experimentally it was found that a correction was still necessary where the frictional losses were low. The sum of the pendulum and indicator losses was plotted on a concentric scale.

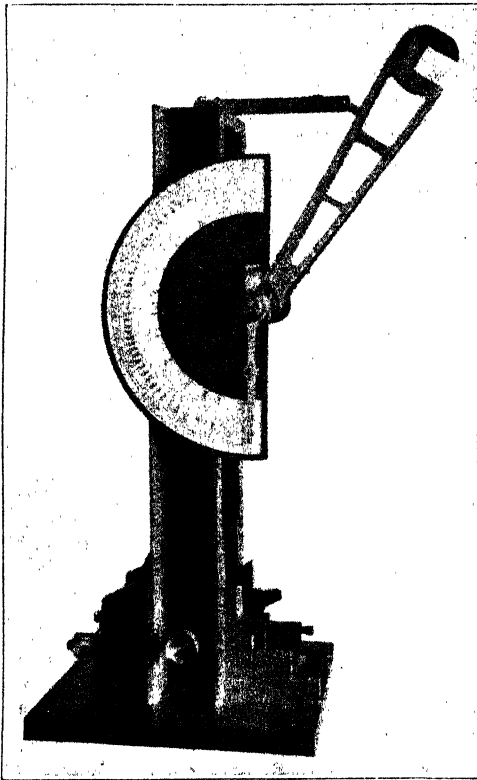



FIG. 41.

After breaking a specimen the frictional loss indicated on the scale was added to the indicated residual energy of the pendulum, giving the true energy. This, subtracted from the applied energy (2·0 ft.-lb.), gives the energy absorbed in breaking the specimen. Variations in the total correction are conveniently allowed for by resetting the indicator spring to give the correct loss on a free swing.

The edges of the L-grips which hold the specimens are rounded to a curvature of ⅛ in. radius, with the arms of the L 90° apart. The striking edge of the pendulum has sides 45° apart rounded to a curvature of ⅛ in. Further details of the adjustable supports are given in the original paper. The supports are suitable for round or square section test-pieces between ½ and 1⅛ in. in size.

Resistance of Pottery to Impact and Chipping.—A similar machine is used for the testing of finished pottery. In its latest form[1] the pendulum is suspended by 8 wires so as to swing true in a vertical plane on a 24 in. radius. A single 5-oz. hammer has two prepared faces, one for impact testing (smashing) and the other for chipping. Full details may be found in the references quoted.

3. *The Rattler Test*

The A.S.T.M. test[2] is designed to indicate the wear due to traffic on a road or pavement composed of paving bricks. The conditions of testing are such that the average percentage loss may reach 22 per cent. for heavy traffic bricks or 24 per cent. for light traffic bricks.

The test consists essentially in rotating ten test bricks in a ball-mill at 29·5 to 30·5 r.p.m. for a total of 1800 revs. Suitable bricks are weighed to the nearest 0·1 lb. In the revised tentative specification[3] four nominal paving brick sizes, from which bricks must not deviate more than ±⅛ in. in transverse dimensions, or ±¼ in. in length exclusive of lugs or bevelled ends. The maximum permissible losses are as given below :—

Transverse Dimensions.	Length.	Loss in Rattler Test.
Inches.	Inches.	Per cent.
2½ × 4	8½	26
3 × 3½	8½	26
3 × 4	8½	24
3½ × 4	8½	22

The bricks are placed in the machine with the weighed and graded charge of balls and the treatment checked by a revolution counter.

[1] *Bur. Stands.*, *Tech. News Bull.*, No. 146, 1929, 56; Anon., *Ceram. Age*, 1929, 14, 205.
[2] Anon., *J. Amer. Ceram. Soc.*, 1928, 11, 480.
[3] A.S.T.M., Ser. Design. C 7-29 T; *Proc. A.S.T.M.*, 1929, 29, Pt. 1, 628.

Ten revs. are allowed for starting and stopping, and if any stoppage occurs during the test, the result must be rejected if it would disqualify the sample. Finally, the weight of all pieces of brick of 1 lb. weight and over is taken, the loss calculated on the total original weight, and the correction applied as given above.

The balls are of cast-iron containing not less than 2·50 per cent. of combined carbon and not more than 0·25 per cent. of graphitic carbon, 1·00 per cent. of silicon, 0·50 per cent. of manganese, 0·25 per cent. of phosphorus and 0·08 per cent. of sulphur. The total weight of balls is to be as near 300 lb. as possible made up as follows:—

Number.	Diameter, ins.	Approximate weight singly.	
		lb.	kg.
10	3·75	7·5	3·40
245-260	1·875	0·95	0·43

The scales on which the weighings are done should be tested by a standard weight at not more than every ten tests. The larger balls are weighed separately after every ten tests and replaced if as low as 7 lb. (3·175 kg.), so long as all the spheres are not changed at once. The aim is to maintain a graduated range of wear. Provided that a graded series is maintained as for the larger balls, the smaller ones are rejected as soon as they will pass through a 1·75-in. hole in a ¼-in. iron plate or weigh less than 0·75 lb. (0·34 kg.). Broken or otherwise defective balls are to be replaced as soon as found.

The parts of the rattler cylinder are illustrated in Fig. 42, and the construction of the machine is as follows:—

"The barrel of the machine shall consist of the heads, headliners, staves and staveliners conforming to the following requirements:

"The heads may be cast in one piece with the trunnions which shall be $2\frac{7}{16}$ in. in diameter, and shall have a bearing 6 in. in length; or they may be cast with heavy hubs which shall be bored out for $2\frac{7}{16}$ in. shafts and shall be keyseated for two keys, each ½ by ⅜ in. and spaced 90° apart. The shaft shall be a snug fit and when keyed shall be entirely free from lost motion. The distance from the end of the shaft or trunnion to the inside face of the head shall be 15⅜ in. inside the head for the driving end of the rattler and 11⅜ in. for the other head, and the distance from the face of the hubs to the inside face of the heads shall be 5⅛ in.

"The heads shall not be less than ¾ nor more than ⅞ in. in thickness. In outline, each head shall be a regular 14-sided polygon inscribed in a circle 28⅜ in. in diameter. Each head shall be provided with flanges not less than ¾ in. in thickness and extending outward 2½ in. from the inside face of the head to afford a means of fastening the staves. The surfaces of the flanges of the head shall be smooth and give a true and uniform bearing for the staves. To secure the desired true and

uniform bearing, the surfaces of the flanges of the head shall either be ground or machined. The flanges shall be slotted on the outer edge, so as to provide for two $\frac{3}{4}$ in. bolts at each end of each stave, the slots to be $\frac{13}{16}$ in. in width and $2\frac{3}{4}$ in. centre to centre. Each slot shall be provided with a recess for the bolt head, which shall act to prevent the turning of the same. Between each two slots there shall be a brace $\frac{3}{8}$ in. in thickness extending down the outward side of the head not less than 2 in.

"There shall be for each head a cast-iron headliner, 1 in. in thickness and conforming to the outline of the head, but inscribed in a circle $28\frac{1}{8}$ in. in diameter. This headliner shall be fastened to the head by seven $\frac{3}{8}$-in. cap screws, through the head from the outside. Whenever these headliners become worn down $\frac{1}{2}$ in. below their initial surface level, at any point of their surface, they shall be replaced with new ones. The metal of these headliners shall be hard machinery iron and should contain not less than 1 per cent. of combined carbon.

"The staves shall be made of 6-in. medium carbon steel structural channels $27\frac{1}{4}$ in. in length and weighing 15·5 lb. per linear foot. The staves shall have two holes $\frac{13}{16}$ in. in diameter drilled in each end, the centre line of the holes being 1 in. from the end and $1\frac{3}{8}$ in. either way from the longitudinal centre line. The spaces between the staves shall be as uniform as practicable, but shall not exceed $\frac{5}{16}$ in.

"The interior or flat side of each stave shall be protected by a liner $\frac{3}{8} \times 5\frac{1}{2} \times 19\frac{3}{4}$ in. The liner shall consist of a medium-carbon steel plate, riveted to the channel by three $\frac{1}{2}$-in. rivets, one of which shall be on the centre line both ways and the other two on the longitudinal centre line spaced 7 in. from the centre each way. The rivet holes shall be countersunk on the face of the liner and the rivets shall be driven hot and chipped off flush with the surface of the liners. These liners shall be inspected from time to time, and if found loose shall be at once reriveted.

"When a new rattler, in which a complete set of new staves is furnished, is first put into operation, it shall be charged with 400 lb. of shot of the same sizes, and in the same proportion as provided" (above), "and shall then be run for 1800 revolutions at the rate of speed specified" above. "The shot shall then be removed and a standard shot charge inserted after which the rattler may be charged with brick for a test.

"No stave shall be used for more than 70 consecutive tests without renewing its lining. Two of the 14 staves shall be removed and relined at a time in such a way that of each pair, one falls on one side of the barrel and the other on the opposite side, and also so that the staves changed shall be consecutive but not contiguous: for example, 1 and 8, 3 and 10, 5 and 12, 7 and 14, 2 and 9, 4 and 11, 6 and 13, etc., to the end that the interior of the barrel at all times shall present the same relative conditions of repair. The changes in the staves should be made at the time when the shot charges are being corrected, and the record must show the number of charges run since the last pair of new-lined staves was placed in position.

"The staves when bolted to the heads shall form a barrel 20 in. in length, inside measurement, between headliners. The liners of the staves shall be so placed as to drop between the headliners. The staves shall be bolted tightly to the heads by four $\frac{3}{4}$-in. bolts and each bolt shall be provided with a locknut and shall be inspected at not less frequent intervals than every fifth test and all nuts kept tight. A record shall be made after each inspection showing in what condition the bolts were found.

"The barrel shall be mounted on a cast-iron frame of sufficient strength and rigidity to support it without undue vibration. It shall rest on a rigid foundation with or without the interposition of wooden plates, and shall be fastened thereto by bolts at not less than four points.

"The barrel shall be driven by gearing whose ratio of driver to driven is not less than one to four. The countershaft upon which the driving pinion is mounted shall

not be less than $1\frac{15}{16}$ in. in diameter, with bearing not less than 6 in. in length. If a belt drive is used, the pulley shall not be less than 18 in. in diameter and $6\frac{1}{2}$ in. in face. A belt at least 6 in. in width, properly adjusted to avoid unnecessary slipping, should be used."

A detailed record-sheet under twenty-four headings and a standard report-sheet, as recommended by the A.S.T.M., is given in the original reference (*loc. cit.*).

4. *Abrasion*

A comparative test which gives some information as to the structure of ceramic materials, particularly of the constructional group such as common and firebricks, is described by L. Bradshaw and W. Emery.[1] Using a Matthewson sand-blast machine, especially adapted for the purpose and with a nozzle of 0·275 in. diameter, the sample is exposed for four minutes to a sand-blast at a constant pressure of 7 lb. per sq. in. and the sand full on. The sample is clamped with its upper face horizontal and 7 in. below the nozzle. Osborn Reynolds[2] has considered the underlying principles and shown that the cutting action does not depend upon the sand being harder than the material cut.

Alternatively,[3] a piece having a grinding surface of 50 sq. cm. may be mounted under a definite pressure on an emery disc of 22 cm. radius driven at 22 r.p.m. and fed with 20 gms. of Naxos emery per minute. The disc should make 450 revolutions during the experiment. The loss may be expressed in gm. or c.c.

Scratch hardness,[4] using Mohr's mineral scale, or a special range of steels, is sometimes a useful test.

W. G. Hancock and W. E. King[5] describe a method of conducting an abrasion test with the test-piece heated in a furnace. A refractory block is driven to and fro by a small motor, suitable standard conditions being chosen. M. L. Hartman and O. A. Hougen[6] also describe abrasion tests at atmospheric and higher temperatures. S. C. Cole[7] proposes a modified rattler test for the resistance of silica bricks to such abrasion as they receive in coke ovens, etc.

Resistance to Weathering

Examination for Detrimental Enclosures

The clays used for heavy products such as bricks, salt-glazed pipes, fireclay goods sometimes contain lumps of calcium carbonate, iron and other sulphides, and calcium sulphate (gypsum). Sorting followed by fine grinding usually reduces trouble from such sources to a negligible point, but this is not always commercially feasible. Weathering of the

[1] *Trans. Ceram. Soc.*, 1920, **19**, 77, 79. [2] *Brit. Assoc. Rep.*, Sect. A, 1873.
[3] *Cf.* Böhme, *Mitt. Königl. Versuchsanstalt*, 1891, 153.
[4] *Cf.* L. Navias, *J. Amer. Ceram. Soc.*, 1929, **12**, 69. [5] *Trans. Ceram. Soc.*, 1923, **22**, 317.
[6] *Trans. Amer. Electrochem. Soc.*, **36** (Cold and Hot abrasion tests).
[7] *Proc. A.S.T.M.*, 1929, **29**, Pt. 1, 288.

clay before use, while assisting in exposing impurities and in developing the plasticity of certain indurated clays, may increase trouble in the manufactured product, owing to soluble salts causing disfiguration and also structural damage due to crystallisation. The conditions under which such damage occurs are complex and still the subject of investigation, notably, in this country, by the Building Research Station at Watford.

Particles of quicklime in the burnt product are particularly injurious and may lead to cracking or blowing off portions of the surface of the goods. A suitable test is to place samples in a saturated atmosphere, as, for instance, under a bell-jar, but out of contact with water, for eight days. Alternatively, samples may be enclosed in a strong container to which superheated steam is admitted, as is commonly done in testing glazed goods for crazing.

Resistance to Frost

Five samples of a convenient size may be taken, saturated with water as for porosity determination, or taken after such a test and frozen for four hours in a freezing bath at -15° or lower, then thawed out in water at 20°. The detached particles should be left behind and the freezing repeated 25 times. The detached particles are then collected, dried and weighed, and the weight expressed as a percentage of the original dry weight.

Thermal and Dielectric Strengths

Tests under this heading include dielectric strength at various temperatures up to 600°, combinations of dielectric stress with stresses set up by rapid warming and cooling, effect on transverse strength of previous heating to 900° and spalling or loss of material consequent on rapid chilling from temperatures such as 1350°. The last test relates chiefly to firebricks, the others to hard porcelain for electrical purposes.

The British Standard Specifications [1] for Electrical Porcelain comprise Type Tests for not less than three insulators of the same size and type, and Routine Tests to be applied to every piece passed for service. These tests apply particularly to insulators for overhead power lines for 3000 to 150,000 volts. The body of the insulator is to be ivory white, sound, free from defects and thoroughly vitrified so that the glaze is not depended upon for insulation. The glaze is to be brown and to cover all exposed parts.

As to electrical design the insulators shall spark over before puncturing and the dry spark-over voltage must be in excess of that under the rain test. The limits of voltage are explained below. The

[1] *British Engineering Standards Assn.*, No. 137, 1922.

insulators must be so designed that, in multi-part insulators, the fall in voltage over individual parts is approximately proportional to their thickness.

From the mechanical point of view, the factor of safety of the assembled insulator under load should be at least 2½, based on the yield-point. The design should be so arranged that stresses due to expansion and contraction do not lead to the development of defects. The porcelain must not engage directly with a hard metal screw thread. For cemented joints, British Standard Portland Cement[1] is recommended. With other cements care should be taken that no chemical action with metal parts ensues, so as to cause a fracture by expansion. Recommendations as to marking are also incorporated in the specification.

TYPE TESTS: *Inherent Stresses.* The insulator, fitted complete as in service, is heated for one hour in a water-bath at 93°.[2] It is then immediately immersed in a mixture of ice and water and left for one hour. The surface is then dried and the piece subjected to the Dry Spark-Over Test given below. This procedure must be repeated three times without the insulator failing, even as to its glaze.

An American specification[3] gives a somewhat similar test but with a temperature range of 100° to 0°, with ten-minute periods in each bath. The treatment is continued on five or more pieces until all have fractured mechanically.

A more drastic test than either of the above is recommended from the same source for Sparking Plug and Heating Device Porcelain. Transverse strength specimens[4] are used, twelve or more being taken. Half of these are tested by central loading on a 5-in. span, the other half are so treated after heating and cooling. They are placed in a furnace and brought to 900° for two hours. They are then cooled, over a period of four hours, to room temperature and tested for transverse strength. The results are reported in detail, the averages calculated and the percentage loss in strength due to the heating and cooling is derived from the averages.

Dry Spark-Over Test. The insulator, complete with its fittings, is tested in a dry state as follows. A 0·4 in. diam. wire is affixed as in service. An alternating current of frequency between 25 and 100 per second and approximately sine-curve form is applied between the wire and the pin or other support. A voltage of about one-third of the full test value is at first applied and this is increased at a rate of about 1 kilovolt per second until spark-over occurs. The voltage at spark-over must not be less than that given in the table on p. 125.

[1] *British Engineering Standards Assn.*, No. 12, 1920.

[2] Modified from 50° C. See *Nature*, 1929, 123, 225.

[3] *J. Amer. Ceram. Soc.*, 1928, 11, 475. [4] *Ibid.*, p. 472.

Table of Test Voltages (R.M.S. Values)

A.C. Voltage Delivered or Declared.	Dry Spark-Over Test.			Rain Test.			Puncture Test.		
	Supporting Insulator.		Tensioning Insulator.	Supporting Insulator.		Tensioning Insulator.	Supporting Insulator.		Tensioning Insulator.
	Pin Type.	Suspension Type.		Pin Type.	Suspension Type.		Pin Type.	Suspension Type.	
Kilovolts	KV	KV	KV	KV	KV	KV	KV	KV	KV
3	40	...	30	20	...	70	70	...	52
6	50	...	40	30	...	20	87	...	70
10	62	...	54	39	...	30	108	...	95
20	95	90	90	62	57	57	166	158	158
30	125	125	125	84	84	84	220	220	220
40	145	150	150	105	105	105	250	260	260
50	158	175	175	125	125	125	275	310	310
60	165	200	200	140	142	142	290	350	350
80	...	250	250	...	180	180	...	440	440
100	...	300	300	...	220	222	...	525	525
120	...	335	335	...	250	260	...	585	585
150	...	365	365	...	315	315	...	610	610

It is also specified, where apparatus is not available for tests in excess of 310 KV., that the separate units of an insulator may be tested individually and the equivalent puncture-test of the complete insulator be estimated from these individual tests.

The test-voltage is measured by a suitable instrument either on the high or the low voltage side of the transformer, calibrated by means of a sphere spark-gap. The data and corrections for such spark gaps are given in an appendix to the specification.

Rain Test. The test is conducted as for the dry spark-over, except that an artificial rain at about 15° is played on the insulator at an angle of about 45°. The rain is adjusted to a rate equivalent to 1 in. in five minutes (5 mm. per min.) and the resistance of the water at 15° is not to be more than 20,000 ohms per cm. cube. The appropriate minimum voltages are given in the table above.

Puncture Test. The insulator is tested as for dry spark-over, except that it is completely immersed in oil during the test, and carried to the voltage at which puncture of the insulator occurs. This value is not to be less than that given in the table above.

Dielectric Strength Tests on Special Test-Pieces as given in the American Specifications[1]

Mechanical Test. An insulator, complete with fittings, is subjected to a gradually increasing load until failure occurs. The conditions

[1] *J. Amer. Ceram. Soc.*, 1928, 11, 474.

of service are simulated. For a pin insulator the load is applied at right angles to the axis of the piece by means of a flexible wire rope loop placed round the neck. Any appreciable permanent set constitutes failure. For tensioning insulators the load is applied between the metal connections on either side. A factor of safety of 2½ is specified and applied to the maximum working load of the range within which the insulator is required to fall. The ranges are:—Up to 400 lb., 400 to 800, 800 to 1400, 1400 to 2000 lb.

Porosity Test. This is given on p. 94.

High Voltage Test. Pin type insulators are inverted in water so as satisfactorily to cover the testing terminal, and any clamp or binder attached to the neck groove and filled with water to the top of the fastening hole. A voltage which just sparks over is applied and maintained for five minutes. The insulator must not puncture under these conditions.

Tensioning insulators are tested with the appropriate spark-over voltage applied for five minutes between the metal connections. Details of frequency and voltage measurement are the same as for the type tests. The insulator must not puncture under these conditions.

Proof Load Test. Tensioning insulators and supporting insulators of the tensioning type are suspended complete, as for service. They must sustain a load 20 per cent. in excess of the maximum working load.

The load is applied vertically by means of a wire attached to the lower fitting of the insulator and maintained for one minute.

The purchaser may require not more than 1 per cent. of pin-type insulators to be tested in the same manner.

Spalling of Firebricks

The following method[1] may be adhered to rigidly, or, for immediate comparative purposes, varied to suit the convenience of the tester.

At least five standard 9-in. bricks or five pieces cut to this shape with a grinding or a "cut-off" wheel are taken. Each brick is weighed and the batch is placed in the doorway of a furnace maintained at 1350° (2462° F.), so that one 4½ × 2½ in. end of each brick is directly heated for one hour. The samples are then taken out and stood on their hot ends in a tank of flowing water at 10 to 20° (50 to 70° F.), the ends being immersed to a depth of 2 in. After three minutes the samples are taken out of the water and allowed to steam for five minutes and then returned to the furnace, the door of which is kept closed whilst the bricks are out. The hourly cycles of heating and cooling are continued until a loss of 20 per cent. in each brick has occurred. When pieces begin to fall off, the sample is laid on a 4½ × 9 in. asbestos

[1] A.S.T.M., Serial Desig., C 38-27 T; Tentative Spec., *J. Amer. Ceram. Soc.*, 1928, 11, 461.

board divided into 100 equal squares and the approximate loss after each cycle estimated. The pieces at the conclusion are weighed and the percentage losses calculated. The report should indicate the number of cycles which the piece sustained before noticeable loss occurred, the per cent. loss after each cooling, and the number of cycles up to a loss of 20 per cent by weight.

One useful variant is to discard the asbestos board, weighing, dry, after each cycle and reporting lost weight, as a percentage for each dipping, up to a loss of 20 per cent.

C. W. Parmelee and E. R. Westman[1] studied the effect of an air-blast on part of a face initially at 1100°, and compared the resulting effect on the transverse strength with the results of other methods of testing.

Reversible Thermal Expansion (Hot and Cold Sizes) of Refractory Materials[2]

Reference should be made to p. 80 for the distinction between this and permanent changes in size. The latter are also dealt with below.

The aim of the present test is to obtain an average rate of expansion on a whole brick; the result being expressed as a change per unit length per degree Centigrade. The experimental data are the lengths of the brick between chosen points at atmospheric temperature and at 1300°. Coppée's apparatus is convenient for the measurements.

Two parallel saw-cuts are made in the 9 in. × 3 in. face of the brick, not less than 1 in. deep and ½ in. from each end. A thick platinum wire with one end finely pointed is fixed in each cut so that the point projects about ¼ in. above the face of the brick. The brick is levelled in a suitable furnace. A horizontal cathetometer is placed 5 or 6 ft. from the brick and adjusted while truly horizontal so that both telescope cross-wires are exactly on the tips of the platinum wires. The instrument is now rotated on its stand so as to focus on a meter scale placed conveniently and the distance between the cross-wires measured. One of the cm. divisions on the scale is made to coincide exactly with the cross-wires. The other telescope is provided with an extra vertical hair-line which travels across the field under the control of a micrometer head. The number of turns required for a travel of 1 mm. on the scale is determined and also the number between the nearest scale division and the cross of the wires. This gives, by proportion, the fractional part of the length. As an example, a length measured in this way is given as 21·636 cm. The same process of measurement is again carried out with the brick at a temperature of 1300°. Alternatively,

[1] C. W. Parmelee and E. R. Westman, *J. Amer. Ceram. Soc.*, 1928, **11**, 884.

[2] *Trans. Ceram. Soc.*, 1918, **17**, 325.

readings may be taken at successive temperatures and plotted graphically.

A suitable furnace has a chamber 24 in. long by 12 in. wide and 9 in. high with two small openings about 8 in. apart for viewing the points. A gas-blast furnace may be used. Viewing at high temperatures, it may be added, is greatly facilitated by the addition of a corresponding pair of holes at the opposite side of the furnace. These may be fitted with mica windows or plugs to be taken out during the short time required for the measurements.

Determination of After-Contraction or After-Expansion of Refractory Materials [1]

The Gas Engineers' Specification demands that the sample be heated to a temperature equivalent to Cone 14 (1410° C., 2570° F.). The sample is, accordingly, heated in a suitable furnace until the required cone squats and then maintained steadily at the maximum temperature for two hours, using a pyrometer to check fluctuations.

The test is carried out on two rectangular pieces about 3 in. by 1 in. to 2 in., by 1 in. to 2 in. One of these is cut across the end of the sample brick and the other across the middle. The sample brick is selected from the middle of the kiln setting. The opposite ends of the test-pieces are ground parallel and the distance between them measured to 0·005 cm. by a vernier gauge. The measurement is repeated on the cooled pieces after the above heat-treatment. A gas-furnace is recommended with air supply under pressure and an oxidising atmosphere.

The limits specified are :—

Silica or siliceous material	0·5 per cent.
Retort material	1·0 ,,
Firebricks, Grade I.	0·75 ,,
Firebricks, Grade II.	1·15 ,,

Many users consider that the test is not sufficiently severe and that the testing temperatures should be raised.

The Identification of Various Forms of Silica in Silica Bricks.[2]

Silica occurs in bricks as quartz, tridymite and cristobalite. The proportions of these in refractory bricks, etc., have considerable bearing on the behaviour of the material in service and on the thoroughness of the firing to which they have been subjected. The properties

[1] *Trans. Ceram. Soc.*, 1918, 17, 320; *Standard Spec. for Refract. Mat. for Gas Works Inst. of Gas Engineers*, revised 1922.

[2] *Trans. Ceram. Soc.*, 1918, 17, 311.

available for their identification are specific gravity, crystalline form and habit and refractive index.

For a separation by specific gravity the finely divided material is suspended in a heavy solution. Bromoform (sp. gr. 2·90) or methylene iodide (sp. gr. 3·33) and solutions of these in benzene are suitable. These may be diluted with benzene in order to obtain optimum density for separation. Quartz is thus separated from the other two forms, but the densities of the latter lie too close for a practical separation.

Crystal form and habit are best examined in thin sections. Again, quartz is readily distinguished, but the distinction between tridymite and cristobalite depends upon the crystal form and mode of twinning of the former being apparent and this is often not the case. Under crossed nicols quartz is again readily distinguished by its birefringence being greater. The following method due to A. Scott appears to give useful results.

Scott's Method. The refractive indices in sodium light are quartz 1·549, tridymite 1·477, cristobalite 1·484. The material is finely powdered in order to separate the minerals and, being immersed in a liquid of known refractive index, is examined microscopically. The Becke bright-line method, commonly used by petrologists, serves to show when the index of refraction of the immersion liquid has been adjusted to the same value as that of the mineral examined. The method of Schröder van der Kolk[1] is considered to be most convenient and sensitive. This method depends upon the relative dispersive powers of the solid and the immersion liquid. The preparation is viewed on a dark ground and illuminated from below by oblique white light from all sides. The mineral is immersed in a solution of mercury potassium iodide of such concentration that tridymite and the solution have identical refractive indices for sodium yellow light. This state of affairs is achieved either by preliminary immersion of a known sample of tridymite or by the use of a refractometer. The preparation is covered with a cover-glass to prevent evaporation. On viewing under the above conditions the cristobalite particles will show orange coloured fringes, the tridymite ultramarine fringes and the quartz white fringes. Mercury potassium iodide (K_2HgI_4) solution should be kept over a little mercury in a well-stoppered bottle. It is a yellowish-green transparent solution which is very poisonous and corrosive to the skin, rubber, etc. It must not be brought in contact with metals other than mercury. Variations in temperature between preparing the solution of required concentration and its use should be guarded against.

[1] Schröder van der Kolk, *Kurze Anleitung zur Mikroskopischen Krystallbestimmungen*, Wiesbaden, 1898; Alan Dick, Appendix to "Kaolin, China Clay and China Stone Handbook," *Mem. Geol. Survey*, 1914.

Expansion curves give useful results (*vide* p. 80) particularly as to the presence and relative amounts of tridymite and cristobalite.

The Action of Flue-Dust and Slags on Refractory Materials

A number of qualitative tests simulating industrial conditions have been proposed. One of the most useful, which does not involve a preliminary destruction of the skin of the brick, is Nesbit and Bell's method.[1] A ring of stoneware approximately 4 in. in diameter and ½ in. thick and deep is cemented by a thin film of fine grog mixed with silicate of soda to the desired face of the test-piece. The receptacle so formed is filled with powdered slag, fired to the desired temperature, *e.g.* Cone 10, retained at that temperature for, say, four hours and then allowed to cool. The cooled piece is sawn across the middle of the slag patch and examined for depth and nature of penetration, and amount of superficial solution, etc.

In addition to the factors involved in the above test, a mechanical factor due to the impact of flue dust on refractories sometimes requires to be taken into account. J. W. Mellor[2] describes a furnace in which the dry powdered slag is introduced from a hopper into the gas-burner. The latter is directed vertically downwards on to the test-piece which is definitely orientated with respect to the burner. The flow of the dust into the burner can be inspected through a glass tube and controlled by means of a conical valve at the base of the hopper and a cut-off tap below this. The method of testing is to place two test-bricks side by side centrally in the bottom of the furnace and with their top faces at a fixed distance from the burner, close up the furnace, raise the temperature steadily to a maximum (1400° is a useful temperature to employ), admit the desired amount of slag (−60's sieve) steadily during the next half-hour with the temperature maintained constant and controlled by a pyrometer and subsequently keep the temperature constant for a further half-hour. A detailed discussion is given in the above reference and by J. W. Mellor and W. Emery.[3]

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GLASS

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THIS section is divided into three parts. In the first, the methods of analysis applied to the very varied raw materials are considered; in the second, the general composition of various types of glass is described, together with notes on the chemical durability of glasses, its effect on their utility and methods for its determination; in the third, the analysis of finished glass products is dealt with in detail.

I.—THE RAW MATERIALS AND THEIR EXAMINATION

Glasses are composed of an acidic oxide, generally silica, but for particular purposes replaced partly in some glasses by boric or phosphoric oxide, and at least two basic oxides, one of which is an alkali oxide and the other an alkaline earth or other metallic oxide such as oxide of lead, zinc or aluminium. A few special optical glasses contain no silica, and others consist of lead oxide and silica only, but these are very exceptional. Various other materials are introduced into glass for specific purposes, such as the production of colour or of opacity, for decolorising, or to assist in the fining of the glass.

The raw materials used in glass manufacture may be roughly classified into six groups under the following headings:—

A. Materials which introduce silica, boric oxide or phosphoric oxide into the glass.
B. Materials which introduce alkali oxides.
C. Materials which introduce alkaline earths or other metallic oxides.
D. Opacifying agents.
E. Colouring and decolorising agents.
F. Miscellaneous raw materials.

Such a classification cannot be rigidly adhered to, as many materials could legitimately be included under more than one heading. Thus bone ash is always used on account of its opacifying properties, but it also introduces into the glass lime and phosphoric oxide.

The mixture of raw materials which, on fusion, produces glass is technically referred to as the "batch." If it is desired to introduce any particular constituent into a glass, either the material itself may be added to the batch or some salt which yields the required material upon decomposition during the fusion process. For instance, to introduce a basic oxide into a glass the oxide itself may be added to the batch or the corresponding hydroxide, carbonate, or nitrate, the quantities of the different materials being calculated to yield the desired amount of oxide after decomposition.

A. Materials which introduce Silica, Boric Oxide or Phosphoric Oxide

1. SILICA

Silica is the chief component of practically all types of glass and may constitute up to 80 per cent. of the finished product. It is usually added to the batch in the form of sand. Other forms of silica may be used, as, for example, crushed quartzite or ground flints, but sand is generally preferred owing to the advantages presented by its physical condition. Natural silicates such as felspar, kaolin, steatite, etc., are frequently used but generally on account of their other constituents and not principally for their silica content.

Sand consists chiefly of silica and is composed of quartz grains with varying amounts of other mineral grains as impurity. The actual grains are frequently coated with a film of clay or other impurity which may be removed to a great extent by suitable washing. Some of the best glassmaking sands, after washing, contain over 99·5 per cent. of silica, and the heavy mineral grains in sands (felspar, rutile, tourmaline, etc.) do not occur to any significant extent. Sea-shore sands frequently contain lime as shell fragments, as much as 30 to 40 per cent. being present on occasion. Clay and felspathic grains occur to a greater or less extent in practically all sands and in the poorer grades of sand the quartz grains are frequently coated with limonite. Small amounts of lime, alumina or alkalis are beneficial rather than deleterious when present as impurities in the sand, especially alumina, which is a desirable constituent of most types of glass. A significant amount of alumina in a glass sand usually indicates the presence of either felspar or clay, and these minerals generally contain iron oxide. If the impurities are present in large quantities, the sand is very liable to be of variable composition.

The most objectionable impurity in a sand required for the manufacture of colourless glass is iron oxide, and in a general sense the value of a sand for glassmaking purposes depends largely upon its freedom from iron. (For the commoner types of coloured glass, iron

oxide in the sand may actually be advantageous.) The amount of iron oxide permissible in a sand for glassmaking purposes depends upon the type of glass for which the sand is to be used and also upon the iron oxide content of the other constituents of the batch. According to Boswell[1] the amount of iron oxide allowable in the sand used should not exceed 0·02 per cent. for optical glasses containing barium and zinc and for crystal glass; 0·04 per cent. for crown optical glass; 0·05 per cent. for laboratory ware and medical glass; 0·05 per cent. for plate glass; and 0·1 per cent. for window glass. In practice these limits may be exceeded slightly if the decolorising is carefully carried out. Sand for the manufacture of common dark bottles, either of green or brown tint, may contain 2 to 3 per cent. of iron oxide and also a significant amount of alumina with advantage.

A rough estimation of the amount of iron oxide in a sand may be formed by calcining a sample and comparing the colour after calcination with that of standard samples of sand of known iron oxide content similarly treated. Good quality sands should remain white after calcination or at the most show only a faint pink tinge. The presence of lime in the sand interferes with this test as the lime exerts a bleaching effect on the colour produced, the maximum effect being exerted when twice as much lime as iron oxide is present.

Very few British glass sands contain less than 0·03 per cent. of iron oxide after washing, and where large deposits of fairly even composition are available the average iron oxide content of the best sands is about 0·04 to 0·05 per cent. after washing. American glass sands are of better average quality. According to Boswell,[2] the average iron oxide content of the best American washed sands is about 0·02 per cent. and the silica content from 99·0 to 99·6 per cent. If the sand is required for the manufacture of colourless glass, the presence of carbonaceous matter is detrimental. Peaty matter is frequently present in the sand to some extent, and coal dust is often acquired from trucks or barges during transport.

Examination of a Sample of Sand

Preliminary Examination:—(1) A sample of the sand is calcined and the colour of the calcined sample noted. (2) Examination with the microscope:—Pure sand should consist of transparent colourless quartz grains. Ferruginous sands are usually coloured yellow to red and the quartz grains coated with clay or limonite. Grains of felspar and mica may usually be readily identified. Heavy detrital minerals frequently show up as dark grains and are undesirable as, besides iron oxide, they may contain titanium oxide (rutile, anatase), zirconia (zircon), etc.; such grains are only fusible in the glass melt with great

[1] *J. Soc. Glass Tech.*, 1917, 1, 7. [2] *Ibid.*, 147.

difficulty and are apt to appear as undissolved grains in the finished glass. (3) A sample of the sand is washed by stirring vigorously in water and allowing to settle. If the supernatant liquid remains turbid, the presence of clay is indicated. (A determination of the amount of iron oxide in the sample before and after washing will indicate the extent to which the sample may be improved by washing.) The presence of peaty matter or carbonaceous impurities such as coal dust, if present, is apparent from the colour of the washing water or the settlement of a dark coloured layer on the surface of the washed sand. (4) A rough test for iron oxide may be made by boiling 10 g. of the sand with hydrochloric acid, diluting to a definite volume, adding potassium thiocyanate solution to an aliquot portion and comparing the colour so obtained with that produced from a sand of known composition after similar treatment.

An exact determination of the composition of a sand can be made by the methods employed for the quantitative analysis of glass (see pp. 228-235). In technical sand analyses the constituents generally determined are silica, alumina, iron oxide, lime and, less frequently, the alkalis and titanium oxide. The iron oxide should be determined on a separate sample as described on p. 170, and titania may be determined colorimetrically as on p. 242. When grinding a sample of sand for analysis, care should be taken that the sample remains representative and that the harder grains, which have a great tendency to fly from the mortar during grinding, are incorporated in the ground sample.

For a rapid analysis, 1 to 5 g. of the ground sample may be weighed out into a large platinum crucible, moistened with water, decomposed with hydrofluoric and sulphuric acids as described in the method for glass analysis (see p. 225) and the bases determined in the usual manner in the resulting solution (see pp. 230-235). The loss on ignition is determined and the silica is obtained by difference. It is essential that a careful blank experiment be carried out with the reagents used, as the impurities contained in these are frequently considerable, even when " pure " reagents are employed.

For routine control of sand supplies a determination of the iron oxide and moisture content of the sand is generally considered sufficient. In works where washed sand is used, it is necessary to make frequent determinations of the moisture content of the sand and adjust the quantity added to the batch accordingly, in order to keep the batch composition constant. If the sand has been dried previously, frequent moisture determinations are unnecessary, but dry sand does not yield such an even batch mixture as sand containing 2 to 3 per cent. of moisture.[1]

[1] Parkin and Turner, *J. Soc. Glass Tech.*, 1926, **10**, 114.

The suitability of any particular sand for glass manufacture, apart from its chemical composition, is determined by its grain size. If the average grain size is too large, or a quantity of large grains is present, the fusion is retarded and incompletely fused grains may be left in the glass causing "sandy" metal. If the sand is too fine—and especially if used in a damp state—fine air bubbles are carried into the glass, and these are very difficult to remove during the melting process in order to obtain plain glass. The ideal glass sand would contain all grains of pure quartz and all of the same size, preferably the medium sand grade (diameter 0·25 to 0·5 mm.).

Fontainebleau sand contains about 70 per cent. of grains of this size and 26 to 28 per cent. of the next lower grade (diameter 0·1 to 0·25 mm.). Lynn sand contains about 95 per cent. of the medium sand grade and 4·5 per cent. of the fine sand grade. The best American glass sands are usually rather coarser in grain, a sample from Ottawa yielding 6·1 per cent. coarse sand grade (diameter 0·5 to 1·0 mm.), 88·4 per cent. of the medium sand grade and 5·1 per cent. of the fine sand grade.[1]

The grading of the sand may be determined by sieving or elutriation. Sieving is satisfactory for the coarser fractions if standard sieves are used. The sieves constructed according to the regulations of the Institution of Mining and Metallurgy have wires of the same diameter as the apertures so that the apertures have a definite size. With such standard sieves reliable information can be obtained as to the grading of a sand. Elutriation is only necessary when it is desired to investigate the fine powder[2] (for methods, see Clays, pp. 37-53).

Quartz is rarely used in glass manufacture. It is a pure form of silica, but in order to use it as a constituent of a glass batch it must be reduced to a powder and this presents difficulties, as, owing to the extreme hardness of the raw material, a considerable amount of iron would be introduced into the ground product through abrasion from the grinding machinery, and even if the grinding were preceded by a preliminary calcination to facilitate pulverisation the resulting product would contain a large proportion of dust and be very unevenly graded. The analysis of quartz and quartzites is conducted in the same manner as the quantitative analysis of a glass sample (see pp. 228-235). As the impurities are usually very small in amount, the sample may be opened up with hydrofluoric and sulphuric acids, the bases determined and the silica obtained by difference (see pp. 225, 235). In preparing the sample for analysis it is advisable to raise it to a red heat and quench it in water previous to grinding, as this facilitates disintegration and a better average sample is obtained.

[1] Boswell, *J. Soc. Glass Tech.*, 1917, 1, 149.

[2] Boswell, *Memoir on British Resources of Sand suitable for Glassmaking:* Longmans, Green & Co., 1916, p. 22.

Flint is seldom used as a source of silica in glass. It is a fairly pure form of silica but it has the same disadvantages as quartz. Grinding would render the product expensive as compared with sand, even if it were otherwise unobjectionable. The colouring matter in flints is chiefly organic and is removed by calcination. The analysis of the calcined product is carried out in the same manner as recommended for quartz samples.

Natural Silicates.—Many natural silicates may be used advantageously in the production of certain types of glass. In England and America the natural silicates in general use are felspar, china clay and clay marls. In America lepidolite has found an increasing use in recent years. On the Continent, trachyte, phonolith, basalt and similar rocks are extensively used in the manufacture of coloured bottle glass. These minerals contain from 50 to 70 per cent. of silica, and in some cases valuable amounts of lime and alkalis, but they are generally added to a glass batch as a cheap and convenient source of alumina.

Certain china clays, lepidolites and felspars are comparatively free from iron oxide and can be used advantageously in the manufacture of colourless glass as a source of alumina since they are much less expensive than calcined or hydrated alumina and are also much more readily incorporated into the glass. Marls and volcanic rocks of the basalt type usually contain so much iron oxide (and other colouring oxides) that they can be used only in the manufacture of coloured bottle glass, for which, however, their low cost and comparatively high alumina content renders them particularly valuable. The analysis of these minerals is conducted according to the methods given for clay (p. 2) or glass (p. 227 *et seq.*).

2. BORIC OXIDE

Boric oxide is a valuable constituent in many types of glass. It has a greater influence than any other oxide in lowering the coefficient of expansion of a glass and is consequently very useful as a batch constituent for types of glass in which low expansion or high thermal endurance is essential; for example, thermometer glass, miners' lamp glass, lamp chimneys, oven ware and laboratory ware. In amounts up to about 10 per cent. of the silica present, boric oxide assists the chemical durability of glass. It is useful in coloured glasses on account of its solvent action on the colouring oxides, and in optical glasses "boric oxide has become essential for all flint glasses intended for shortening the secondary spectrum."[1] A few special borate crown glasses contain no silica but have boric or boric and phosphoric oxides as the only acidic oxides. Such glasses, however, are not durable and are only designed for special optical purposes.

[1] *Jena Glass*, Hovestadt. Trans. by Everett, p. 9: Macmillan & Co., Ltd., 1902.

Boric oxide is generally introduced into glass by means of boric acid or borax, either crystalline or anhydrous. On account of the large percentage of water of crystallisation in crystal borax ($Na_2B_4O_7 . 10 H_2O$ = 47·1 per cent. H_2O) borax glass is generally used in pot furnaces, for if crystal borax is used the water of crystallisation which is driven off at an early stage leads to excessive frothing during the fusion process. Natural borates such as borocalcite, boronatrocalcite and boracite (borates of calcium, calcium and sodium, and magnesium respectively) are seldom employed as they generally contain too much iron oxide for use in making colourless glass.

Boric Acid is generally used as refined boric acid containing about 99 per cent. H_3BO_3, the crude commercial acid containing 80 to 90 per cent. H_3BO_3 being seldom used. The refined acid contains a little hygroscopic water, small amounts of sulphate, chloride and insoluble matter and slight traces of iron.

The crude acid contains hygroscopic water (1 to 7 per cent.) and, sometimes, considerable amounts of impurities such as alkali sulphates and chlorides, silica, organic matter, sulphuric acid, ferric oxide, alumina, lime and magnesia. Boric acid is soluble and most of these impurities are insoluble in absolute alcohol so that a determination of the hygroscopic moisture and the residue insoluble in absolute alcohol gives approximately the boric acid content by difference. The hygroscopic water is determined by drying the sample for two hours at 50° and then for twelve hours over concentrated sulphuric acid. The dried sample is then dissolved in absolute alcohol and the insoluble impurities filtered off through glass wool in a Konink filter tube which is dried to constant weight before and after the filtration by drawing air at 50° through it. The impurities are not completely insoluble in absolute alcohol and the hygroscopic water is not completely removed at 50°, so the results given for the boric acid content are usually about 2 per cent. too high. The method serves, however, for technical control of supplies.

Determination of the Impurities. From 2 to 5 g. of the dried sample is dissolved in hot water, the insoluble impurities filtered off and the filtrate acidified with nitric acid. Half the solution is then evaporated to dryness, after the addition of methyl alcohol (to drive off the boric oxide as volatile methyl borate), the dry residue taken up with a little hot dilute hydrochloric acid and the silica—if present—filtered off, ignited and weighed. In the other half of the solution, sulphate and chloride are determined in the usual manner. For the determination of the bases a second sample is evaporated to dryness with hydrofluoric acid and a few drops of sulphuric acid. The boric acid is thus expelled as volatile boron trifluoride. (The addition of a further quantity of hydrofluoric acid and repetition of the evapora-

tion is advisable to ensure the complete volatilisation of the boron.) The dry residue is taken up with water and hydrochloric acid, and the solution divided into two parts. The oxides of aluminium, iron, calcium and magnesium are determined in one part and the alkalis in the second part.

A direct determination of the boric acid in the sample may be made volumetrically by titrating an aqueous solution of the material with standard sodium hydroxide solution using phenolphthalein as indicator. Sodium meta-borate is formed according to the equation:— $H_3BO_3 + NaOH = NaBO_2 + 2H_2O$. The pink colour becomes apparent before all the boric acid is neutralised, as sodium meta-borate is slightly hydrolysed. This hydrolysis is prevented if glycerol or mannitol in sufficient quantity is added to the solution, and the boric acid can then be completely neutralised before a permanent colour appears. The procedure is as follows:—5 to 10 g. of the boric acid sample is dissolved in hot water and the solution made up to 500 c.c. An aliquot part of this solution is transferred to an Erlenmeyer flask, glycerol or mannitol added, and the solution titrated with $N/2$ sodium hydroxide solution using phenolphthalein as indicator. When the pink colour appears a further quantity of glycerol or mannitol is added and, if the colour disappears, the addition of the standard alkali continued until the solution again becomes pink. The addition of glycerol or mannitol and the titration are repeated alternately until the colour of the solution remains permanent after a fresh addition. This indicates the completion of the neutralisation, and the amount of boric acid present in the solution can be calculated from the volume of standard alkali added. (1 c.c. of $N/2$ sodium hydroxide = 0·031 g. H_3BO_3.)

Mannitol is usually preferred to glycerol on account of greater convenience in handling. If glycerol is used it should be carefully examined for the presence of free acid which, if present, must be neutralised with dilute sodium hydroxide. The standard sodium hydroxide solution must be free from carbonate, as this interferes with the reaction,[1] and it should be standardised by means of pure fused boric oxide, or by pure crystal borax according to the method given below for borax.

For the technical control of refined boric acid it is generally sufficient to determine hygroscopic moisture, insoluble matter, sulphate and chloride, and to calculate the boric acid as difference.

Borax.—For routine control of borax supplies, determinations of hygroscopic moisture, insoluble matter, sulphates and chlorides should be made. Calcined borax is hygroscopic and the moisture content, therefore, very variable. The moisture is determined by heating a

[1] See Mellor, *A Treatise on Quantitative Inorganic Analysis*, 1913, p. 579.

weighed sample in a platinum crucible, gently at first, and finally at a dull red heat. The loss in weight is moisture. If the sample contains any colouring oxides as impurity, their presence will be indicated in the fusion. The most likely adulterant is sodium carbonate, which may readily be detected by the addition of dilute acid.

The direct determination of the sodium oxide and boric oxide in borax may be made volumetrically. Free boric acid has no action on methyl orange or *p*-nitrophenol, so that if hydrochloric acid be added to an aqueous solution of borax it will only react acid to either of the indicators named when all the soda has been neutralised and all the boric acid is free. The free boric acid can then be titrated with standard alkali, using phenolphthalein as indicator, as described above for boric acid. The actual procedure is as follows :—10 g. of the borax sample is dissolved in air-free distilled water and the solution made up to 500 c.c. or 1 litre. An aliquot part is pipetted into an Erlenmeyer flask, a drop of *p*-nitrophenol solution added and standard $N/2$ hydrochloric acid run in until the yellow colour is just discharged. From the amount of acid required, the amount of sodium oxide in the sample can be calculated. (1 c.c. of $N/2$ acid = 0·0155 g. Na_2O).

An equal aliquot portion of the borax solution is then taken and the required amount of acid (as ascertained above) added to neutralise the sodium oxide and liberate the boric acid. Mannitol or glycerol is added and a few drops of phenolphthalein solution, and the titration completed as described above under boric acid. (1 c.c. of $N/2$ sodium hydroxide = 0·0175 g. B_2O_3.)

The two above titrations may be carried out in the same solution if desired. The sodium oxide is first titrated with standard acid, using *p*-nitrophenol as indicator, and when the neutralisation point is reached, the alkali titration for boric oxide is commenced. The first drop of standard sodium hydroxide solution should restore the yellow colour, and the burette reading is *then* noted. Phenolphthalein and mannitol (or glycerin) are added and the yellow colour disappears, because mannitol (or glycerin) forms an acid of sufficient strength with boric acid to affect *p*-nitrophenol indicator, although boric acid alone does not. The titration is then completed as above. As the titration proceeds the yellow colour reappears and grows stronger, becoming intense just before the phenolphthalein end-point appears. This latter is first noticed as a faint brownish tinge and with one further drop of sodium hydroxide solution it is changed to an intensely brownish red, which is the real end-point.

If the borate contains carbonate as impurity, the sample is neutralised with hydrochloric acid as above and the carbon dioxide removed by boiling after connecting to a reflux condenser to prevent

the volatilisation in steam of any of the boric acid, before proceeding with the titration for boric oxide.

3. PHOSPHORIC OXIDE

Phosphoric oxide is used as an essential constituent in the manufacture of certain types of opal glasses and of special optical glasses (phosphate crown) and is occasionally found in small quantity in some varieties of crystal glass. When used as constituent of opal glass the phosphoric acid is usually added as some form of calcium phosphate (see Opacifying Agents, p. 157).

In the phosphate crown glasses, the form in which the phosphoric acid is added depends upon the composition of the glass desired. If the phosphoric oxide content is comparatively low, the whole of the phosphoric acid may be added as a salt of some basic oxide which it is also desired to introduce into the glass (usually a neutral alkali phosphate Na_2HPO_4 or K_2HPO_4), but if the phosphoric oxide is high in comparison with the bases (on occasion 60 to 70 per cent. P_2O_5 in the glass) the excess is added in the form of metaphosphoric acid. The alkali phosphates are used to introduce the small amounts of phosphoric oxide sometimes found in crystal glass. Whatever the raw material used, the main purpose of the analysis is to check the moisture, phosphoric oxide and iron oxide content, and basic oxide, if present, the usual methods being employed.

B. Materials which introduce Alkali Oxides

The chief alkali oxides occurring in glass are those of sodium and potassium, and, to a much smaller extent, lithia. The materials used to introduce these oxides into glass generally have a comparatively low melting-point and therefore facilitate the melting operations in glass manufacture, and for this reason they are classified as fluxes. Generally speaking, the greater the percentage of alkali contained in the batch, the more readily will it melt and "plain," that is, become clear and free from undissolved particles (stones) and bubbles of gas (seeds). There is a limit to the amount of alkali which may be added to the batch, since glasses containing a high percentage of alkali oxide are not chemically durable in use (see p. 190), though they are easier to manufacture.

1. SODIUM OXIDE

The batch materials in common use which introduce sodium oxide into glass, either alone or in conjunction with other oxides, are the carbonate, sulphate, and nitrate of sodium, borax (used chiefly for its boric oxide content, see p. 139) and certain silicates such as the soda or soda-potash felspars which are generally used as a cheap

means of introducing alumina into glass. Sodium is also introduced into glass by means of cryolite and sodium silicofluoride, which are used as opacifying agents (see p. 157).

Sodium chloride is very seldom used as a batch material, as it is volatile at the temperature of the glass furnace and escapes without decomposition. Commercial sulphate, carbonate and nitrate of sodium usually contain a small amount of chloride as impurity, and if this is not in excess of, say, 1 per cent., it is useful in a lime glass in assisting the plaining of the glass, owing to the stirring effect produced by its volatilisation at high temperature. Small amounts of sodium chloride may remain dissolved in the glass.

Sodium Carbonate—Soda Ash—is frequently referred to in glass works as "alkali." It is the batch material most widely used for the introduction of sodium oxide into glass, and is chiefly used in conjunction with lime, less frequently with lead oxide. Soda ash made either by the Leblanc process or by the Solvay (Ammonia-Soda) or other processes may be used for glassmaking, but the latter is generally preferred on account of its greater purity. The soda ash may be "light" or "heavy" quality, both varieties being obtainable of equal purity, the only difference being in the volume weight of the product. The "heavy" ash is preferable on account of its greater density as it is not so dusty in use and so gives rise to less loss through fine powder being carried away (particularly in a tank furnace), and it also yields a denser batch mixture which has a greater heat conductivity than the batch produced when the "light" ash is used.

Soda ash is fairly hygroscopic and consequently regular moisture determinations should be made in order to keep the alkali content of the batch constant. Soda ash has been found to contain over 20 per cent. of moisture after long storage, but the average amount of moisture present in fresh deliveries of heavy soda varies from 2 to 5 per cent. and is usually about 3 to 3½ per cent.

Commercial soda ash is usually very pure. The impurities present are insoluble matter, sodium sulphate, sodium chloride and iron oxide. Sodium bicarbonate may also be present. The iron oxide is included with the insoluble matter on the solution of the sample, the amount being determined as described on p. 169. If the soda ash is to be used in the manufacture of a heavy lead glass, the determination of the chloride and sulphate is important as, if present in any quantity, these impurities cause the glass to become milky or opalescent.[1] The complete examination of sodium carbonate is carried out according to the methods given in Vol. I., p. 554.

A special grade of soda ash containing from 8 to 10 per cent. of

[1] Cauwood and Turner, *J. Soc. Glass Tech.*, 1917, 1, 87, and Fenner and Ferguson, *J. Amer. Ceram. Soc.*, 1918, 1, 468 and 561.

sodium sulphate is sometimes manufactured for the use of glass-makers, as some are of the opinion that a proportion of sodium sulphate in the batch yields a better quality of glass.

Sodium Sulphate—Saltcake—has long been used in the glass industry as a source of sodium oxide, especially in the manufacture of sheet, plate and bottle glass. Most of the saltcake used for glass-making is manufactured by the Leblanc process, but some is manufactured by the Hargreaves-Robinson process. In recent years the quality of saltcake has improved considerably as regards freedom from free acid and iron. Further, pure anhydrous sodium sulphate, obtained by the dehydration of the crystallised salt, is now obtainable, and this material in conjunction with soda ash is very suitable for the manufacture of colourless glass in tank furnaces. Saltcake may be used alone or in conjunction with soda ash. Carbon is sometimes added to saltcake batches to facilitate decomposition of the saltcake. Powdered coal, coke, anthracite, or charcoal may be used for this purpose, the amount required being about 5 per cent. of the saltcake present. When saltcake is added to a glass batch, some of it is usually found in solution in the resulting glass.

The chief impurities in saltcake are insoluble matter, free sulphuric acid (as acid sulphate), calcium sulphate, sodium chloride and iron (partly as oxide and partly as sulphate). The complete analysis of saltcake is carried out as described in Vol. I., p. 509. For the routine control of saltcake supplies, the most important determinations are moisture, insoluble matter, sodium chloride, free acid and total iron in the consignment as received, with periodical checks to determine the increase in moisture if the saltcake remains in stock over a considerable period. Powdered anhydrous saltcake absorbs moisture fairly readily, and if stored in a damp place for any considerable time becomes very hard and lumpy. If this occurs, it is necessary to grind the hard lumps of saltcake, determine the average moisture content and make due allowance for the amount to be added to the batch. As a rough check for determining the increase in the moisture in saltcake which has been stored, the loss on gentle ignition of the stored material can be compared with the loss on gentle ignition of the material as received, the difference representing the increase in moisture content. The total iron can be determined as described on p. 169.

A form of sodium sulphate recovered as a by-product in the manufacture of chromium compounds is used for making green (actinic) glasses. This contains from 1 to 2 per cent. of sodium bichromate. To determine the amount of chromic acid present, the aqueous solution of the "chrome salt" (as the product is called) after filtration from the insoluble matter is acidified with hydrochloric acid and an acid solution of potassium iodide (10 per cent.) added. The chromic acid is reduced

to a chromium salt with the liberation of an equivalent amount of iodine, which is titrated with a standard solution of sodium thiosulphate.

Sodium Nitrate is chiefly used in glass batches as an oxidising agent. It introduces sodium oxide into the glass, but for this purpose only is much more expensive than soda ash. Sodium nitrate melts at a lower temperature than soda ash and is sometimes used to replace part of the soda ash in refractory glass batches to facilitate fusion. The material generally used is refined nitrate of soda. The impurities commonly present are insoluble matter, chloride and sulphate of sodium, and iron oxide. The total iron oxide present is determined as described on p. 169, and chloride and sulphate in the usual manner. For the complete examination of sodium nitrate see Vol. I., p. 472. As sodium nitrate is hygroscopic, fairly frequent moisture determinations are necessary.

2. POTASSIUM OXIDE

Potassium oxide is used either wholly or partly as a substitute for sodium oxide as the alkali oxide in glass. Though more expensive than sodium oxide, its special properties render it of particular importance in certain types of glass. It is generally used together with lead oxide in the manufacture of the best crystal glasses, as potash glasses can be obtained more free from colour than soda glasses. The principal materials used for the introduction of potassium oxide into glass are the carbonate and nitrate of potassium and potash felspar.

Potassium Carbonate technically referred to as "potash" may be used in the anhydrous or the hydrated form, the former being generally used in Great Britain. Hydrated potash may contain 1½ (17·4 per cent.) or 2 (20·7 per cent.) molecules of water. The purity of potassium carbonate depends upon its origin and method of preparation: the material obtained as a by-product from sugar manufacture (melassen pottasche) which is used extensively in Continental Europe may contain up to 10 per cent. of sodium carbonate. Average supplies of potash contain only small amounts of chlorides, sulphates, sodium carbonate and insoluble matter. Sodium carbonate is not deleterious in itself, unless a pure potash glass is desired for special purposes. Chlorides and sulphates are objectionable as, if present in any considerable amount, they give rise to milky and opalescent glass.[1] Certain varieties of potassium carbonate may contain phosphate, for example, Russian potash. The insoluble matter, if present to any significant extent, must be examined for iron (see p. 169), and owing to

[1] Cauwood and Turner, *J. Soc. Glass Tech.*, 1917, 1, 87; and Fenner and Ferguson, *J. Amer. Ceram. Soc.*, 1918, 1, 468 and 561.

the exceedingly hygroscopic nature of potassium carbonate, moisture determinations must be made at frequent intervals in order to keep the amount of potassium oxide in the glass batch constant.

The complete analysis of potassium carbonate is carried out as described in Vol. II., p. 424.

Potassium Nitrate, "Nitre" or "Saltpetre," is very frequently used as the source of a part of the potash in heavy lead glasses, its principal function being to ensure the prevention of reduction of the lead oxide during the fusion of the batch, though its oxidising properties are useful generally, and it is a valuable constituent of batches for glasses which are either coloured by manganese or in which manganese is used as the decolorising agent (see p. 166). There is a limit to the amount of saltpetre that can be added advantageously to a glass batch, as excess causes undue frothing during melting. It is added to the batch as "refined saltpetre" which is obtainable in a high degree of purity. Potassium nitrate is less hygroscopic than sodium nitrate, but the moisture determination is of importance. Insoluble matter, sulphates and chlorides are usually present in negligible quantity, if at all. For the examination of potassium nitrate see Vol. II., p. 420.

Potash Felspar is used in many types of glass and furnishes a useful source of alkali oxides. It is generally added to a batch on account of its alumina content (see p. 151). The important factors to observe in felspar supplies are the alumina and alkali contents and especially the iron, either present in combination in the felspar or introduced as metallic powder during the grinding. The quality of a felspar sample can be ascertained only by a complete analysis, which is carried out as for clay (see p. 17) or for glass (p. 228).

3. LITHIUM OXIDE

Lithium oxide is introduced into a few special glasses, such as glass for the "windows" of X-ray tubes,[1] and is generally added to the batch as lithium carbonate. For more common glasses, lepidolite (lithia mica) is used as a substitute for felspar, particularly in the United States. Lepidolite is preferable to felspar in that it forms a batch which is more readily fusible; it is also usually less contaminated with iron. The general examination of lithia-containing batch materials is carried out by the methods employed for the corresponding potash materials, the lithium being determined by the Gooch method[2] in the mixture of alkaline chlorides obtained in the Lawrence Smith determination for alkalies (see p. 235).

[1] Powell, *J. Soc. Glass Tech.*, 1918, 2, 245.

[2] See Mellor, *A Treatise on Quantitative Inorganic Analysis*, 1913, p. 536; Hillebrand, *Bulletin* 700, *U.S. Geol. Survey*, 1919, p. 212.

C. Materials which introduce Alkaline Earths and other Metallic Oxides

Under this heading may be considered batch materials used for introducing the oxides of calcium, barium, magnesium, lead, aluminium and zinc.

1. CALCIUM OXIDE

Calcium oxide is the cheapest basic oxide available for the manufacture of durable glass and is present together with soda in all the cheaper types of glass, such as window glass, bottle glass, etc. The batch materials used for introducing lime into glass are (1) various forms of calcium carbonate, either natural (such as limestone, limespar, chalk, marble, etc.) or artificial (precipitated as a by-product in certain chemical operations), (2) burnt and slaked lime and (3) in conjunction with magnesia as dolomitic limestone or dolomite, either natural or burnt, if magnesia is not undesirable. Calcium fluoride (fluorspar) and calcium phosphate are also used in glass manufacture, but chiefly as opacifying agents and are referred to later under that heading (see p. 153). In England some form of calcium carbonate is generally used, but in America burnt and slaked lime are frequently employed. The relative advantages and disadvantages as batch constituents of the carbonate, oxide and hydroxide of calcium have been discussed by Hodkin and Turner.[1]

Calcium Carbonate.—Natural forms of this material require grinding in order to ensure efficient mixing with the other batch materials and also to facilitate decomposition during melting. The degree of fineness to which it must be ground depends upon the method and rate at which the melting process is carried out. For tank furnaces working at full capacity, the mineral should be ground to pass through a screen with 8 holes to the linear inch, but where the output of the tank is appreciably below its full melting capacity, more coarsely ground material is permissible—say, ground to pass a $\frac{1}{4}$ inch mesh. For pot furnace working, finer grinding is advisable—say, $\frac{1}{16}$ to $\frac{1}{20}$ inch mesh. A suggested specification for limestone (also burnt and slaked lime) for use in glass manufacture has been proposed by the U.S. Bureau of Standards.[2] It deals with sampling and analytical methods, chemical compositions for different grades and fineness of grinding.

Ground limestone is the material most commonly used for introducing lime into glass. The colour of the material—white, light grey cream or yellowish—gives an indication of its purity. Dark coloured limestones frequently owe their colouring to organic matter and may have a comparatively low iron oxide content, but if the organic

[1] *J. Soc. Glass Tech.*, 1921, 5. 341. [2] *Glass Industry*, 1922, 3, 54.

matter is appreciable they are unsuitable for the manufacture of colourless glass, as carbon interferes with decolorising. For the best qualities of glass, calcspar (frequently called limespar) is preferred to limestone as it can be obtained of greater average purity. The chief impurities in limestone are iron (either present as oxide or carbonate in the natural mineral or introduced in the metallic form during grinding), silica, alumina, magnesia, sulphur trioxide, organic matter and, less frequently, manganese oxide and calcium fluoride. In a general way, the value of a sample of limestone (or calcspar) for glassmaking depends upon its calcium carbonate and iron contents, the importance of the latter depending upon the type of glass to be made. For colourless glass the amount of iron oxide permissible in the ground material depends upon the iron oxide present in the other materials with which it is mixed in the batch; but it should not exceed 0·05 per cent., whereas for common dark bottle glass the presence of iron is advantageous rather than otherwise.[1] Alumina is an impurity in the sense that it is not calcium carbonate. Actually its presence may be advantageous rather than deleterious (see p. 151).

For routine control the following determinations are sufficient:—(1) calcspar and good quality limestones: iron oxide and moisture; (2) medium quality limestones: iron oxide, moisture, matter insoluble in hydrochloric acid, and alumina; (3) impure limestones usually require more extended tests owing to their variability in composition. The iron oxide is determined as described on p. 169. The complete analysis is carried out according to the method given on p. 19 *et seq.*

Ground chalk is not extensively used in glassmaking. The natural material has to be dried before grinding and the drying process frequently introduces cinders. The average iron oxide content of ground chalk is higher than that of good quality limestone, and chippings of flint pebbles are frequently found. As the moisture content is usually appreciable and variable, frequent determinations of it are necessary. The general examination is the same as for limestone.

In some localities precipitated calcium carbonate by-products are used for glass manufacture. These by-products are obtained from such chemical industries as soap, paper and gas manufacture and from tar oil works and water softening plants. They usually contain appreciable quantities of moisture and, in addition to the impurities originally present in the lime before its conversion to carbonate, they also contain impurities peculiar to the particular industry from which they are obtained. For example, the material from gas works contains excessive sulphate and that from tar oil works organic compounds which may cause an intended pale green glass to be coloured amber if melted at a comparatively low temperature.

[1] See Dimbleby and Turner, *J. Soc. Glass Tech.*, 1922, **6**, 221.

Burnt and Slaked Lime.—Burnt lime in lumps is usually purer than the crushed limestone from the same quarry unless the latter is specially selected. It requires grinding before use and is unpleasant to handle. It also absorbs moisture and carbon dioxide from the air and is consequently of variable composition. Frequent determinations of the loss on ignition are necessary to control the constancy of the batch composition. If the lime is slaked it falls to powder and the expense of grinding is avoided. Slaked lime is better to handle and less variable in composition than burnt lime, but frequent determinations of loss on ignition are advisable. The impurities are the same as those present in limestone and they are determined in the same manner.

Dolomite and Dolomitic Limestone are used when lime and magnesia are introduced together. They are dealt with under magnesia, p. 149.

2. BARIUM OXIDE

Barium oxide is used as a substitute for lime in certain types of glass, either wholly or in part. It is a particularly valuable constituent in some optical glasses, and is frequently present in pressed glass, as it imparts brilliancy to the glass and causes it to set quickly after moulding and so take sharp impressions from the moulds.

The batch materials employed for the introduction of barium oxide into glass are barium carbonate (either natural witherite or the precipitated product), and for special optical glass, the hydroxide or nitrate of barium. The latter are too expensive for use in ordinary glasses.

The impurities found in barium carbonate are the same as in calcium carbonate except that lime is regarded as an impurity. The value of a sample of barium carbonate for glassmaking purposes depends chiefly upon its barium carbonate content and its freedom from iron. Barium sulphate, present to a greater or less extent in most samples, is an undesirable impurity, especially for optical glass. Moisture and loss on ignition (the latter representing organic matter and carbon dioxide from calcium carbonate) are determined in the usual manner. Another (dried) sample is treated with hot dilute hydrochloric acid and any "insoluble matter" filtered off, washed, ignited and weighed. It consists chiefly of silica and barium sulphate and, after determining the total, the silica is removed by evaporation with hydrofluoric and sulphuric acids, the residue usually being taken as barium sulphate. (If an exact analysis is required, the residue is fused with sodium carbonate, the melt extracted with hot water, and the solution, which may contain soluble sulphates, filtered off. After thorough washing, the residue, which contains any barium present as carbonate, is dissolved in hot dilute hydrochloric acid and the barium

precipitated and determined as sulphate in the usual manner.) The barium present in the soluble portion is determined by precipitation as sulphate in the filtrate from the "insoluble matter" and any impurities such as alumina, iron oxide, lime and magnesia are determined in the filtrate from the barium sulphate (see barium glasses, p. 260). It is best to determine the iron in a separate sample (see p. 169).

Occasionally samples of barium carbonate contain minute traces of cobalt, which may easily be overlooked in the course of the analysis unless specially sought, and yet be sufficient to give a glass a bluish tint when colourless glass is desired. The cobalt may be detected as follows:—Five to 10 g. of the sample is treated with hydrochloric acid, the barium removed as sulphate, the alumina precipitated from the filtrate and reprecipitated by the acetate method. The two filtrates from the alumina precipitate are combined and sulphuretted hydrogen passed into the warm slightly alkaline solution. A slight black precipitate is formed if cobalt is present (or a dark brown solution which deposits a fine black precipitate on rendering slightly acid with acetic acid and warming, if the amount of cobalt is very slight) and it is tested in a borax bead to confirm the presence of cobalt.

3. MAGNESIUM OXIDE

Glasses containing magnesia and lime as the basic oxides are superior in certain respects to glasses containing only one or the other of these oxides.[1] For such glasses the batch material usually employed for introducing magnesia and lime together is dolomite or dolomitic limestone, either in its natural state or calcined and subsequently slaked. Supplies of natural dolomite which are sufficiently free from iron oxide for colourless glass do not occur in Great Britain to any extent, but are available in America and are sometimes used instead of limestone for this purpose. Dolomite is frequently used in Great Britain for coloured or pale green bottle glass. It is important to know both the magnesia and lime content of dolomites or dolomitic limestones used for glassmaking because the amount of each oxide introduced into the batch must be kept constant. The chief impurities in these materials are similar to those in limestone and their examination is carried out in a similar manner.

Ground magnesite and calcined magnesia, the latter for better quality glasses, are also used for introducing magnesia into glass. The value of these materials for glassmaking depends upon their freedom from iron and their magnesia content. Their examination is carried out by methods similar to those used for dolomite, but in this case lime

[1] Dimbleby, Hodkin and Turner, *J. Soc. Glass Tech.*, 1921, 5, 352; English and Turner, *ibid.*, 1921, 5, 357.

is regarded as an impurity and special care is taken during the analysis to ensure a complete separation of lime and magnesia. The iron is preferably determined in a separate sample as described on p. 169. Ground magnesite and calcined magnesia should be examined for metallic iron by means of a magnet since there is occasionally present 5 to 6 per cent., derived from the grinding machinery. For the detailed examination, see p. 19 *et seq.*

4. LEAD OXIDE

Lead oxide is particularly valuable as a batch constituent in that it yields glasses of high brilliancy and long-working range. "Full crystal" glasses, such as are usually employed for decorative cutting, are silicates of lead and potassium. In "half-crystal" glasses, the lead oxide is replaced in part by barium or calcium oxide and the potassium oxide partly or wholly by sodium oxide. Glass for electric lighting bulbs usually contains lead.

Red lead is almost invariably used as the batch material for the introduction of lead oxide into glass. Lead peroxide and litharge may be used but are not so suitable as red lead, the former on economic grounds and the latter because it frequently contains metallic lead and also is more liable to reduction in the fusion process, thus involving greater risk of the resulting glass being discoloured. As red lead is generally used in the manufacture of the highest class of glass, it is essential that it should be free from impurities, particularly these which impart colour to glass, such as the oxides of iron and copper. A special quality "for glassmakers" has generally a high grade of purity but "painters'" red lead may contain large amounts of adulterants. The impurities most frequently found are insoluble matter (generally refractory material from the furnace, introduced during the manufacturing process, but occasionally ground red brick as an adulterant, lead sulphate and, especially in painters' lead, barium sulphate), and traces of iron oxide, copper oxide and alumina. Some samples of red lead contain a certain amount of metallic lead, introduced during manufacture, in the form of small globules. Metallic lead is very undesirable as it does not enter into the composition of the glass, thus causing a deficiency in the estimated lead oxide content, and it also tends to hasten the destruction of the "pot" in which the batch is melted. Its presence can be detected by levigation. Commercial red lead frequently contains a considerable amount of moisture, and this should be determined by drying a sample at 110° to constant weight.

The examination of a sample of red lead is carried out as follows:—Five to 10 g. of the dried sample is dissolved by treating with about 10 c.c. strong nitric acid (sp. gr. 1·4) and a little water with the gradual addition of about 2 c.c. hydrogen peroxide (30 per cent.) or a few

crystals of oxalic acid. After the addition of 30 to 40 c.c. of water, the solution is heated on a water-bath for about an hour and allowed to stand for a further hour. The insoluble residue is then filtered off, washed with hot water, ignited and weighed. (If the residue is of significant amount, it should be fused with sodium carbonate or treated with hydrofluoric and sulphuric acids and investigated by the methods employed for lead and barium glasses; see p. 256). The lead is precipitated in the filtrate by the addition of 6 to 8 c.c. sulphuric acid (1 : 1) and the solution evaporated until dense fumes of sulphuric acid are evolved. The solution is cooled, diluted with five times its bulk of water and allowed to stand for some hours, preferably in ice water. The lead sulphate is filtered off through a Gooch crucible, washed with cold dilute sulphuric acid and finally with alcohol, and then dried and weighed. The precipitate, after weighing, is treated with a hot solution of ammonium acetate, in which it should be completely soluble. Any portion remaining undissolved is probably barium sulphate derived from soluble barium compounds in the red lead. The filtrate from the lead sulphate is divided into two parts. In one part the iron is determined colorimetrically (see p. 171) and in the other part, the other metals in the usual manner, special attention being paid to the detection and determination of traces of copper, if present.[1]

It is sometimes desirable to determine the amount of excess oxygen in the red lead, *i.e.* the amount of oxygen combined as Pb_2O_3 or PbO_2. This can be done by warming a weighed quantity of the dried sample with dilute nitric acid (1 : 5), until the soluble portion is dissolved and then adding a definite amount of $N/5$ oxalic acid solution, heating to boiling and titrating the excess oxalic acid with standard potassium permanganate solution (1 c.c. $N/5$ oxalic acid solution = 0·0239 g. PbO_2).[2]

The volatile matter in red lead or other lead oxides can be determined by fusing a weighed amount of the dried sample with about one-third its weight of pure ignited silica for twenty minutes at 800° and a further fifteen minutes at 1000°.[3]

5. ALUMINIUM OXIDE

Alumina increases the strength and durability of glasses and hinders the tendency to devitrification, especially in those containing a high percentage of lime. It is thus a very valuable constituent of many glasses such as bottle glass, glass for laboratory ware, etc. The

[1] See *Colorimetric Method for the Determination of Copper and Iron Oxides*, B. S. White, *Chem. News*, 1916, 114, 214; *cf.* this work, Vol. II., p. 187.

[2] For details see Treadwell and Hall, *Analytical Chemistry*, Vol. II., 1919, p. 623; Mellor, *Treatise on Quantitative Inorganic Analysis*, 1913, p. 323.

[3] O. Andersen, *J. Amer. Ceram. Soc.*, 1919, 2, 10.

influence of alumina on the properties of glass has been discussed in detail in a series of papers by Dimbleby, Hodkin and Turner,[1] and by English and Turner.[2] The particular batch material used for the introduction of alumina into glass depends upon the type of glass in question. Alumina, either calcined or in the hydrated form, is used for particular glasses in which freedom from colour is essential, but it is too expensive for general use and therefore alumina-containing minerals are used for the cheaper varieties of glass.

Calcined alumina is usually fairly pure, but should be tested for "loss on ignition" and for iron oxide. The latter can be determined by fusing a sample with potassium bisulphate or pyrosulphate, dissolving the resulting cake in water and a little sulphuric acid and determining the iron colorimetrically in the resulting solution as described on p. 171. Hydrated alumina is of variable composition and yields a "loss on ignition" varying from 35 to 55 per cent. (combined and hygroscopic moisture and carbon dioxide). The determination of the loss on ignition is therefore important, as is also that of the iron oxide content, which can be carried out as above.[3]

Kaolin (china clay) felspar and lepidolite (the last chiefly in America) are used fairly frequently for introducing alumina into glass. Each of these minerals contains silica in addition to the alumina, so that the amount of sand added to the batch must be reduced accordingly. Felspar and lepidolite also contain alkali oxides which are valuable as batch constituents. Kaolin is rarely used as it is difficult to mix thoroughly with the other batch constituents on account of its physical condition. A complete analysis of these minerals is necessary if they are used for glassmaking, as they vary considerably in composition. The analysis is carried out as described on pp. 2 *et seq.*; 17.

The value of a sample of felspar or similar mineral for the manufacture of colourless glass depends upon its freedom from iron and upon the amount of alkali oxides and alumina which it contains. The iron oxide content is not important in the manufacture of common dark bottle glass, and cheaper grades of mineral may then be used. A review of British sources of felspar supplies considered from the glassmaking point of view has been given by Boswell.[4] Felspar is also used in conjunction with fluorspar in the manufacture of opal glass (see p. 153).

Cryolite, $AlF_3 . 3NaF$, is also used in the manufacture of opal glass and is referred to later (see p. 157).

[1] *J. Soc. Glass Tech.*, 1921, 5, 107. [2] *Ibid.*, pp. 115, 183, 277.

[3] For the complete analysis of hydrated and calcined alumina, see Mellor, *A Treatise on Quantitative Inorganic Analysis*, 1913, p. 447.

[4] *J. Soc. Glass Tech.*, 1918, 2, 35.

6. ZINC OXIDE

Zinc oxide is a valuable constituent of certain types of glass, especially of resistant glass for laboratory ware; it is almost invariably added to a glass batch as such. There are various grades of zinc oxide on the market, the price depending largely upon the colour of the product. For glassmaking a slightly discoloured oxide is not objectionable provided it contains no metallic oxides which would colour the glass. Determinations of moisture, loss on ignition and iron oxide (see p. 169) are usually sufficient for routine control. The amount of zinc oxide in a sample can be determined according to Tambon[1] by digesting, say, 10 g. of the dried sample with 300 c.c. of a solution made up of equal volumes of ammonia (sp. gr. 0·924), ammonium carbonate solution (20 per cent.) and ammonium chloride solution (20 per cent.). After shaking vigorously and allowing to settle, the insoluble residue is filtered off, washed, dried and weighed. The difference between the weights of the original sample and the dried residue represents zinc oxide. The complete analysis of zinc oxide is rarely necessary but if required can be carried out as described for "Paints," Vol. II., p. 449.[2]

D. Opacifying Agents

Opal glasses, or glasses with varying degrees of translucency, are produced by the addition to the glass batch of one or more materials which lead to the separation throughout the glass of opaque, undissolved particles, the separation usually taking place during the cooling of the molten glass and its degree depending to a considerable extent upon the rate of cooling

The principal materials used for this purpose are:—

1. Natural or artificial materials containing fluorine, especially cryolite, fluorspar and the alkali silicofluorides.
2. Mixtures of fluorides with aluminium compounds, felspar and fluorspar being the usual combination.
3. Natural or artificial phosphates; *e.g.* calcium phosphate, bone ash, guano, etc.
4. Tin oxide and zirconium compounds.
5. Talc, asbestos, arsenic oxide, alkali chlorides and sulphates are occasionally used as auxiliary opacifying agents.

The raw material used most extensively in glass manufacture as an opacifying agent is fluorspar, usually in conjunction with felspar.

[1] *Bull. Soc. Chim.*, 1907 [4], 1, 823.

[2] See also Mellor, *A Treatise on Quantitative Inorganic Analysis*, 1913, p. 369; Treadwell and Hall, *Chemical Analysis*, 1919, p. 140; and Scott, *Standard Methods of Chemical Analysis*, 1918, p. 627.

Fluorspar is also used in small proportions in some glass batches as a flux or fining agent, but as its use increases corrosion of the refractory material of the melting chamber, it is to be discouraged except as an opacifying agent.

Fluorspar.—Calcium fluoride, CaF_2. The value of a sample of fluorspar for glassmaking purposes depends chiefly upon a high calcium fluoride content and freedom from iron compounds. Commercial samples usually contain carbonate and sulphate of calcium, silica, clay and occasionally barium and lead compounds as impurities. The colour of the sample is not a reliable guide to its purity, as some comparatively highly coloured samples owe their colour to organic impurity and not to iron oxide. A rough estimation of the quality of a sample may be obtained by observing its colour after calcination at a dull red heat, though this test is not always reliable, as some samples are comparatively highly coloured after calcination owing to the presence of small quantities of manganese.

The accurate analysis of fluorspar, cryolite or similar fluorine minerals is tedious on account of the difficulty of determining accurately the fluorine and silica.

Fluorine. If samples of fluorspar or cryolite are regularly examined, or if a number of samples are to be analysed, the fluorine may be determined directly by mixing the finely ground and dried material with pure dry powdered silica and distilling off the fluorine, as silicon tetrafluoride, with strong sulphuric acid. The volume of the silicon tetrafluoride evolved is measured and its fluorine content calculated.[1] Where only occasional samples call for examination it is generally more convenient to determine the fluorine as calcium fluoride, according to the Berzelius method (see p. 262). The complete analysis (except the fluorine determination) of a sample of fluorspar is carried out as follows:—

Moisture. The ground sample is dried at 110° to constant weight and the loss noted.

Loss on Ignition. Organic matter and carbon dioxide are determined by igniting a weighed quantity of the dried sample to constant weight.

Calcium carbonate is determined by treating a weighed quantity of the dried sample with acetic acid, evaporating to dryness on a water-bath, taking up the residue with 75 per cent. alcohol and filtering. After washing the residue with 75 per cent. alcohol, the filter paper is burned off at as low a temperature as possible and the residue weighed. The loss is reported as calcium carbonate. As calcium

[1] For details of the distillation process see Hempel and Scheffler, *Z. anorg. Chemie*, 1899, **20**, 1; Hempel's *Gas Analysis*, trans. by Dennis, 1911, p. 378; Mellor, *Treatise on Quantitative Inorganic Analysis*, 1913, p. 646; or Treadwell, *Analytical Chemistry*, 1919, **II**, 829.

fluoride is slightly soluble in acetic acid, the actual loss found is rather greater than the amount of carbonate present. Bidtel[1] says that this treatment dissolves 0·0015 g. in each gram of calcium fluoride.

Sulphates and chlorides are best determined in a separate sample by fusing with six times its weight of sodium carbonate, extracting the mass with hot water, filtering and determining sulphur trioxide and chlorine as barium sulphate and silver chloride respectively in aliquot parts of the filtrate, by methods similar to those used for the determination of sulphur trioxide and chlorine in glass (see p. 239).

Silica and the bases are determined as described under the analysis of opal glass (see p. 262), except that in the analysis of fluorspar it is always necessary to add an accurately weighed amount of pure precipitated silica (1·5 to 2 g. per gram of sample) to the fluorspar before mixing with sodium carbonate (6 to 8 g.) to ensure decomposition of the calcium fluoride. The weight of silica added must be deducted from that of the silica eventually determined to arrive at the percentage present in the sample.

Iron oxide may be determined colorimetrically in the alumina precipitate (obtained in the analysis for silica and the bases) after fusing the ignited precipitate with potassium pyrosulphate and dissolving up the resulting cake in water and a little sulphuric acid. This method, however, gives results affected by the iron invariably present in all the reagents used and necessitates a cumbersome blank analysis, so that for an accurate determination of the iron oxide it is preferable to evaporate a separate sample of the dried material almost to dryness two or three times (or sufficient times to expel all the fluorine) with sulphuric acid and a few drops of nitric acid, dissolve the resulting residue in water and a little hydrochloric acid, filter from any undissolved calcium sulphate into a graduated flask, and determine the iron colorimetrically as described on p. 171.

An alternative method for the analysis of fluorspar is given by Gifford[2] and is as follows:—One g. of the finely powdered sample is heated for one hour on a water-bath with 10 c.c. of 10 per cent. acetic acid in an Erlenmeyer flask, into the neck of which a small funnel is inserted to prevent loss by spirting. Silica and the fluorides are only slightly affected, but carbonates of calcium and magnesium and some of the iron oxide and alumina pass into solution as acetates. The mixture is filtered, the residue washed thoroughly with hot water and reserved. The filtrate is acidified with sulphuric acid and evaporated to dryness, any calcium fluoride present being converted into calcium sulphate. The mass is taken up with a small amount of hydrochloric acid, lead (if present) precipitated by hydrogen sulphide and filtered off, to be determined as sulphate (see p. 257). After the hydrogen

[1] *Ind. Eng. Chem.*, 1912, 4, 201. [2] *Ibid.*, 1923, 15, 526.

sulphide has been expelled by boiling, the filtrate is oxidised with nitric acid and the iron oxide, alumina, lime and magnesia determined in the usual manner. From the lime content 0·0011 g. is subtracted—the equivalent of the calcium fluoride dissolved. The residual lime and the magnesia are calculated to carbonates.

The residue from the acetic acid treatment is ignited gently to constant weight and the weight noted. The ignited residue is evaporated to dryness twice with hydrofluoric acid, then moistened with hydrofluoric acid and aqueous ammonia and again evaporated to dryness to convert fluorides of iron and aluminium into oxides, ignited gently and again weighed. The loss in weight is reported as silica. The residue is then treated with 5 c.c. concentrated sulphuric acid and evaporated to dryness very cautiously, the process being repeated to ensure the conversion of all the fluorides present to sulphates. The residue is heated to redness, cooled and boiled with dilute hydrochloric acid containing a little sulphuric acid (0·5 per cent.). Any insoluble matter is filtered off, washed, ignited and weighed as barium sulphate. This is treated again with a few drops of sulphuric acid, ignited and re-weighed. If any change in weight occurs, it indicates that the conversion of fluorides to sulphates has been incomplete.

The filtrate is neutralised with ammonia, 5 c.c. of hydrochloric acid added and hydrogen sulphide passed into the solution to precipitate any lead present. If a precipitate appears it is filtered off, washed and the lead determined as sulphate (see p. 257). The filtrate from the lead sulphide is boiled until all the hydrogen sulphide is expelled, oxidised with nitric acid, and iron and alumina determined in the usual manner (see p. 230). If zinc is present it is precipitated by hydrogen sulphide, filtered off, the precipitate washed, dissolved in hydrochloric acid and the zinc determined as pyrophosphate (see p. 247). If zinc is present in any appreciable quantity, the iron oxide and alumina must be separated by the acetate process and not by ammonia (see p. 246). Calcium and magnesium are determined in the filtrate from the zinc sulphide in the usual manner (see p. 233) and the amounts found calculated to fluorides. To the lime so found must be added 0·0011 g., previously subtracted from the calcium carbonate determined. The amounts of lead, iron, alumina, etc., found in the acetic acid extract of the sample must be added to those found in the analysis of the residue to arrive at the composition of the sample. As iron oxide is a very objectionable constituent, it should be determined on a separate sample by decomposition with sulphuric acid (as described above).

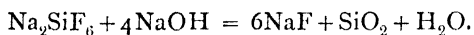
The above method gives quite reliable results for the analysis of commercial samples of fluorspar.

Cryolite, a double fluoride of sodium and aluminium which is found native in Greenland, was formerly used to a considerable extent in the glass industry as an opacifying agent. In recent years consumption has diminished greatly on account of the cost of the material. Natural cryolite has the approximate composition, 60 per cent. sodium fluoride and 40 per cent. aluminium fluoride, with an average iron oxide content of about 0·2 per cent.

The value of cryolite as a constituent of a glass batch depends upon its fluorine content and its freedom from iron oxide. The iron oxide may be determined by evaporating 1 g. of the finely ground mineral almost to dryness with sulphuric acid, repeating the treatment until all the fluorine is expelled. The residue is dissolved in water acidified with hydrochloric acid, and the iron determined colorimetrically (see p. 171). The bases may also be determined in a sample decomposed with sulphuric acid, and fluorine is determined gravimetrically as calcium fluoride by the method described on p. 262 or by the distillation method referred to on p. 154.

Many "cryolite substitutes" are offered for sale, and these consist in general of mixtures of fluorine compounds, including fluorspar and sodium silicofluoride, and compounds of alumina, such as felspar and kaolin, with frequently an addition of sodium carbonate. Such artificial mixtures may be tested by the procedures given above for cryolite, any sodium carbonate present being extracted with water and determined titrimetrically with standard acid.

Sodium Silicofluoride may be tested by titration with standard alkali; 5 g. of the sample is dissolved in boiling water, filtered and the filtrate made up to 250 or 500 c.c. An aliquot part of this solution (25 or 50 c.c.) is heated with 10 c.c. $N/2$ calcium chloride solution and titrated hot with normal sodium hydroxide solution, using phenolphthalein as indicator. The reaction is represented by the equation:—

$$Na_2SiF_6 + 4NaOH = 6NaF + SiO_2 + H_2O.$$

1 c.c. normal sodium hydroxide solution is equivalent to 0·047 g. sodium silicofluoride.[1]

If the insoluble residue is small, the above determination and an iron determination usually suffice for control purposes. Iron oxide is preferably determined in a sample decomposed with hydrofluoric and sulphuric acids (with a small amount of nitric acid also present), the procedure being the same as that described for a glass (see p. 237).

If necessary, a complete analysis of the material may be carried out by the methods described on p. 262 for opal glass containing fluorine.

Calcium Phosphate $Ca_3(PO_4)_2$ is used for the production of opal glasses. It may be added to the batch in the form of bone ash,

[1] Hileman, *Z. anorg. Chem.*, 1906, **51**, 159.

Baker guano, precipitated calcium phosphate, or as ground natural calcium phosphate (apatite). The value of a particular material as an opacifying agent is determined by its actual calcium phosphate content, and its comparative freedom from iron oxide (which adversely affects the colour of the glass when present to an appreciable extent).

The iron oxide in the material may be determined by dissolving say 1 g. of the sample in hydrochloric acid, filtering off the insoluble residue, drying and igniting. The ignited residue is fused with a little pure sodium carbonate, the melt taken up with dilute hydrochloric acid and added to the filtrate from the insoluble residue, the combined solutions then being made up to a definite volume and the iron determined colorimetrically in an aliquot part of this solution by the method described on p. 171.

The complete analysis of calcium phosphate samples can be carried out as described under Fertilisers, pp. 514 *et seq.*; 542.

Tin Oxide is not used extensively as an opacifying agent, but it gives in lead glasses a very dense opal, opaque even in thin sections, and particularly useful for such purposes as opal-backed thermometer tubing, Schellbach burette tubing, etc. Good commercial samples of tin oxide usually have a high degree of purity. The examination is conducted as follows:—"Loss on ignition" is determined by heating a weighed sample in an open porcelain crucible until of constant weight. The loss usually represents moisture. (In rare cases, a negative loss—*i.e.*, an actual gain in weight—may occur. This indicates the presence of particles of metallic tin in the sample.)

The actual tin oxide content of the sample may be determined by evaporating, say, 1 g. of the sample to dryness three times with strong nitric acid. The residue is taken up with hot water and a little nitric acid, filtered, washed and dried. The precipitate is removed from the filter paper as completely as possible and the filter paper burned off separately in a weighed porcelain crucible. The ash is moistened with a few drops of strong nitric acid, evaporated to dryness and ignited. The tin oxide precipitate is added to the contents of the crucible and the whole then ignited to constant weight.

A direct determination of the tin may be made by fusing a dried sample with five times its weight of pure potassium cyanide in a porcelain crucible. A bead of metallic tin is formed (or several small beads, which may be caused to coalesce by gently tapping the crucible) at the bottom of the melt. After cooling, the potassium cyanide is dissolved in hot water and the metallic bead thoroughly washed. It may then be dried and weighed as metallic tin, or may be dissolved in hydrochloric acid and the tin determined volumetrically, using the necessary precautions to ensure that all the tin is obtained as stannous chloride.

The bead may be examined for the presence of other metals (such as lead or copper) and, if present, their amounts may be determined by the usual methods employed for analysing metallic tin (*cf.* Vol. II., p. 264).

Zirconia (ZrO_2) is occasionally used as an opacifying agent in the manufacture of opal glasses. It is usually added in the form of prepared zirconium oxide, or as a trade product sold as "terrar" which consists chiefly of zirconium silicate. In suspension in fused silicates, zirconia has approximately the same opacifying power as tin oxide, and at the present time it is considerably cheaper.

The value of a sample for the production of opal glass depends principally upon (*a*) its zirconia content, and (*b*) its freedom from colouring oxides, particularly iron oxide.

The examination of a sample is conducted by fusing 2 g. with 10 to 12 g. of pure sodium carbonate, leaching the fusion with hot water containing a few drops of alcohol, filtering and washing the insoluble residue thoroughly with hot dilute sodium hydroxide solution. All the zirconia is retained in the precipitate. The precipitate is washed off into a porcelain basin by means of a wash-bottle containing dilute sulphuric acid, the mixture digested on a water-bath and finally filtered through the same filter paper. The filtrate contains most of the zirconium and all the iron. The residue is ignited in a platinum crucible, silica removed by evaporation with hydrofluoric and sulphuric acids, the remaining residue taken up with hot dilute sulphuric acid and filtered.

The two above-mentioned sulphuric acid filtrates are combined, excess sulphuric acid evaporated off, and the solution cooled and diluted until it contains not more than 1 per cent. free sulphuric acid. Hydrogen peroxide is added to this solution to oxidise any titanium which may be present, and then sufficient acid sodium phosphate to precipitate the zirconium as phosphate. After standing at least twenty-four hours, the precipitate is filtered off, washed with water containing a little hydrogen peroxide, ignited and weighed as zirconium pyrophosphate.[1]

Iron oxide may be determined colorimetrically (see p. 171) either in the filtrate from the zirconium phosphate or in a separate sample opened up by fusion with potassium pyrosulphate.

E. Colouring and Decolorising Agents

As a rule the materials used in the glass industry as colouring agents are metallic oxides or their compounds, though exceptions occur as in the case of carbon, sulphur, selenium, etc. For the

[1] For details of the method and separation of other rare earths if present, see Treadwell and Hall, *Analytical Chemistry*, 1919, II, 505; Mellor, *Quantitative Inorganic Analysis*, 1913, p. 508; Scott, *Standard Methods of Chemical Analysis*, 1918, p. 496.

production of particular coloured glasses, colouring agents may be summarised briefly as follows:—

For Blue Glasses. The oxides of cobalt, cupric oxide, and in rare cases (with special treatment), gold.

For Green Glasses. Chromium oxide (as such or as chromates or bichromates), and iron oxide under reducing conditions. Uranium oxide or a chromate in conjunction with cupric or cobalt oxide are sometimes used for green tints.

For Brown and Amber Glasses. Oxides of iron and manganese together under oxidising conditions, sulphur and carbon.

For Yellow Glasses. Cadmium sulphide, uranium oxide, sulphur, and silver compounds.

For Red Glasses. Cuprous oxide under reducing conditions, selenium and gold.

For the production of blue glasses with a purple tint, nickel oxide is very useful, but in potash glasses only. In soda glasses it yields bluish-brown tints, and grey or black glasses in combination with other colouring agents.

For decolorising, selenium, manganese oxide and nickel oxide are used, generally in conjunction with a small amount of cobalt oxide, the particular agent employed depending on the type of glass to be decolorised and its method of manufacture.

For the complete analysis of metallic oxides used as colouring agents, the methods employed are similar to those used for the analysis of the corresponding metals and alloys (*cf.* Vol. II., pp. 1-356). The methods used for such of these materials as are used for paint pigments are described in Vol. II., pp. 467-558. The following notes indicate the main items to be taken into consideration when examining these materials.

Cobalt Compounds.—The materials most generally used are the black and grey (prepared) oxides. The black oxide is of rather indefinite composition, but should contain at least 70 per cent metallic cobalt. The grey (prepared) oxide approximates closely to the composition Co_3O_4. The brands of cobalt oxide generally met with in commerce do not, as a rule, contain more than 1·0 to 1·5 per cent. impurity as iron oxide, nickel oxide and (at the present time, rarely) manganese oxide.

As the colouring power of cobalt oxide is so intense, a small amount of impurity is without noticeable effect in glass manufacture. A rough test may be made by dissolving a sample of the cobalt material in hot strong hydrochloric acid. If the resulting solution is blue, the cobalt is reasonably free from nickel and iron oxides, but if green or greenish, further investigation is called for.

The grey oxide has a greater colouring power than the black oxide of a similar grade of purity, owing to its higher content of CoO. It

happens occasionally that in the calcination of the black oxide to the grey, some of the latter is further reduced to metallic cobalt, so that a sample of grey oxide may have a high cobalt content and yet be definitely inferior to one showing a lower figure, since not only has metallic cobalt no colouring effect but may, if in any appreciable quantity, affect a glass pot adversely.

When very small quantities of cobalt oxide are required in a batch (usually as a decoloriser), it may be added in the form of "powder blue," which is a blue glass, coloured with cobalt oxide and pulverised for use. Its value depends upon its content of cobalt monoxide which can only be determined by a complete analysis of the silicate (see p. 272). Cobalt phosphate is occasionally used in the production of delicate shades of blue.

Copper Compounds produce blue, green or red glasses according to the conditions of manufacture and the nature of the glass batch. Where a blue tint is desired, *black copper oxide* (CuO) is the batch material generally used. The purity of the tint is affected by the presence of iron oxide, which should always be tested for by dissolving up a sample in hot nitric acid, filtering off any insoluble residue and washing with hot water. The filtrate is treated with an excess of ammonium hydroxide whereby the copper first precipitated is redissolved and the iron remains as hydroxide which is filtered off. The precipitate is redissolved with hot dilute hydrochloric acid, reprecipitated with an excess of ammonia solution, filtered and washed rapidly with a hot 2 per cent. solution of ammonium nitrate. The precipitate is then ignited, fused with potassium pyrosulphate and the iron determined colorimetrically as on p. 171.

Copper sulphate is occasionally used as a colouring agent, probably on account of its freedom from iron, as otherwise there is nothing to say in its favour. Its analysis presents no difficulties (*cf.* Vol. II., p. 387).

Cuprous oxide is used in combination with reducing agents (ferrous salts and tartrates) in the production of copper red glasses. The material used should have a high cuprous content and a low cupric one. The analysis presents no special difficulty.

Nickel Compounds are infrequently used as colouring agents, though in potash glasses nickel oxide yields a rich violet-blue colour. The compounds used in glassmaking are the green hydroxide, the black sesquioxide Ni_2O_3, or (most usually) the greenish-grey oxide, NiO. The colouring value depends upon the content of NiO, and therefore the loss on ignition should be determined. If the ignited sample is reduced to metallic nickel in a current of hydrogen, the further loss in weight should be 21·69 per cent. Samples may be contaminated with lime, and if found in a qualitative test, any lime present may be washed out from the reduced metal by acetic acid and

determined after precipitation as oxalate in the usual manner (see p. 233).

Chromium Compounds. — Green chromium oxide, Cr_2O_3, is frequently used. On account of its low solubility in glass it must be used in a finely ground condition (generally water-ground). It is prepared by burning together a mixture of alkali dichromate with from one-fifth to one-quarter its weight of sulphur and washing out the alkali sulphate so produced. The commercial product is usually technically pure, but should be tested for sulphate and unreduced dichromate by washing a sample thoroughly with hot water and determining sulphate (as $BaSO_4$) and chromate (volumetrically) in the filtrate from the chromium oxide.

Potassium dichromate is the agent most frequently used in the production of chromium green glasses. It should always be in a finely ground state—*e.g.* ground to pass a sieve with 30 holes to the linear inch—to avoid the production of black specks so frequently seen in chromium green glasses. If used in the ordinary type of pot flint batch, *i.e.* one containing a small amount of sodium nitrate, the colour produced is a greenish yellow. To obtain clear "actinic" green glass, the batch must contain no oxidising agents and the dichromate must be mixed with about 20 per cent. of a reducing agent such as sulphur or, preferably, powdered charcoal. Sodium dichromate is cheaper than the potassium salt but is more hygroscopic and less easy to deal with satisfactorily in the batch mixing. Commercial dichromates are usually technically pure. If necessary, they may be examined volumetrically in the usual manner. If the sodium compound is used, frequent tests of the hygroscopic moisture are advisable.

The chromates of lead and barium are occasionally used. Chrome iron ore is a cheap source of chromium for green glasses but it is very refractory and requires to be in a very fine state of division if "black specks" (due to undissolved chromium oxide) are to be avoided. The valuable constituent in chrome iron ore is the chromium oxide, which may be determined as on p. 277.

In the manufacture of cheap green bottle-glass, "chrome salt" is sometimes used. This is sodium sulphate containing 1·5 to 2 per cent. of dichromate, and is a by-product in dichromate manufacture. The chromium content may be determined volumetrically in the usual manner.

Numerous very attractive shades of green may be obtained by the combination of the blue produced by copper or cobalt compounds with the yellow tint produced by potassium dichromate (under oxidising conditions) or uranium oxide in varying proportions.

Iron Compounds.—Under reducing conditions iron oxide produces green glasses, but the colours so obtained are not attractive and are

used only for the production of cheap bottle-glasses. The iron is not usually introduced as a separate constituent but as impurity in the other materials used—*e.g.* cheap grades of sand, limestone and natural minerals of the felspathic variety including basalt, whinstone, and even, at times, ground bricks or tiles.

Under oxidising conditions, iron oxide produces brownish-yellow glasses and in conjunction with manganese oxide gives a range of amber glasses varying from almost yellow to a deep purple-brown tint. The iron oxide may be added as the red (Fe_2O_3) or black (Fe_3O_4) oxide, or as a natural mineral such as ochre, sienna, or a good grade of ground hematite. The examination of such minerals is carried out as for iron ores (see Vol. II., pp. 3-34 ; 491).

Manganese Compounds.—The oxides of manganese, under oxidising conditions and in glasses comparatively free from iron, produce a range of colours varying from almost a pink to a violet-purple. The colours are much more satisfactory in potash glasses, the tints being much browner in soda glasses. The material usually used is ground pyrolusite (MnO_2) though the other oxides Mn_2O_3 and Mn_3O_4 may be used. The value of a sample of manganese dioxide for glass-making purposes depends upon the use for which it is required. If for amber glass, a sample with 65 to 70 per cent. or more MnO_2 and about 5 per cent. ferric oxide is usually the cheapest, but for decolorising or for making some of the delicate violet shades the iron oxide should not exceed 0·5 per cent. If the total amount of the manganese oxide present in a sample is to be determined, it is necessary to proceed with a gravimetric separation by the basic acetate method (see p. 245). For the estimation of the peroxides by the determination of the available oxygen, the authors recommend the method given by Barnebey.[1] A ferrous sulphate solution is prepared by dissolving 90 g. crystallised ferrous sulphate in 900 c.c. water and 200 c.c. of strong sulphuric acid, stirring well and cooling. This solution is standardised against a solution of potassium permanganate containing 10 g. per litre, which has previously been standardised accurately by means of sodium oxalate. To carry out the determination, 0·5 g. of the finely ground manganese sample is introduced into a 250 c.c. Erlenmeyer flask, 50 c.c. of the standard ferrous sulphate solution added, the flask covered with a watch-glass or small funnel, and the contents heated to boiling until solution of the ore is complete, after which the solution is diluted to about 150 c.c. and titrated with the standard permanganate solution.

Sulphur in glass batches free from oxidising agents produces a fine amber colour which at times almost approaches red. Crushed roll sulphur, flowers of sulphur, or ground natural sulphur may be used.

[1] *Ind. Eng. Chem.*, 1927, 9, 961.

For control purposes an examination of any mineral residue left after burning off the sulphur from a weighed sample is adequate. The residue should not (and very rarely does) contain any colouring oxides.

Carbon, either alone or in conjunction with sulphur, produces many shades varying from pale amber to dark brown. It is added in the form of graphite, hard-wood charcoal (ground finely) or even ground coke or coal dust, and the glasses are made under reducing conditions. As with sulphur, ignition of a dry weighed sample and examination of the residue is adequate for control purposes.

Cadmium Sulphide produces intense yellow colours in suitable glass batches which are free from oxidising agents. It is customary to add a little free sulphur to the batch in addition to the cadmium sulphide. In making selenium ruby glasses, a proportion of cadmium sulphide is almost invariably added with the selenium.

Cadmium sulphide is prepared from the metal and does not usually contain deleterious impurities, but special care should be taken to see that the sample is entirely free from nitrates (derived from the nitric acid in which the cadmium is dissolved), by boiling it with water for some time, filtering off the solution and testing this for nitrate by the brown ring test, after cooling.

Uranium Compounds.—Uranium oxide produces in lime-soda glasses a greenish yellow fluorescent colour and in heavy lead glasses a light or dark yellow according to the amount present. The material used is usually "Uranium Yellow," frequently sold under the name of "Uranium Oxide" but which is really an acid sodium uranate. Its colouring power depends upon the amount of uranium oxide present. It should be examined for loss on ignition, sodium sulphate, calcium carbonate, or if "uranium orange" is in question, for lead carbonate, as impurity. If a direct determination of the uranium oxide is desired, it is precipitated by ammonia as ammonium uranate and (*a*) gently ignited and weighed as U_3O_8, or (*b*) heated to constant weight in a current of hydrogen and weighed as UO_2.[1]

Selenium, either as selenium powder or as sodium selenite, is largely used in the production of pink and red glasses, usually in conjunction with cadmium sulphide and arsenic. Selenites may be examined for their selenium content by dissolving a weighed quantity of the sample in 1 in 3 hydrochloric acid, saturating the solution thoroughly with sulphur dioxide and boiling. The selenium separates out, is filtered off through a Gooch crucible, washed with water and alcohol, dried at 105° and weighed. (Alternatively, the selenium may be precipitated from the hydrochloric acid solution of the selenite by boiling for fifteen minutes with an excess of potassium iodide.)

[1] For details of this process see:—Treadwell (Hall), *Analytical Chemistry*, 1919, II, 106; Mellor, *Treatise on Quantitative Inorganic Analysis*, 1913, p. 488.

Selenium powder may be examined by driving off the volatile constituents (selenium and possibly arsenic) and examining any non-volatile residue qualitatively. If a determination of the selenium content is desired, it may be carried out as follows:—

According to Meyer,[1] selenious acid solutions cannot be evaporated to dryness without loss, and in the presence of hydrochloric acid that loss may be very large and it is not measurably reduced by the presence of alkali chlorides. On the other hand, it is found that it is not necessary to expel nitric acid from solutions of selenious acid before proceeding to precipitate selenium by means of a reducing agent; it suffices to neutralise the nitric acid with ammonia and reacidify with hydrochloric acid. The selenium content of commercial selenium powders is, therefore, best determined as follows:—0·5 g. of the dried, finely ground powder is weighed out and transferred to a 100 c.c. beaker, 2 c.c. of concentrated nitric acid added, the beaker covered with a clock-glass, placed on a hot plate and gently heated until all the selenium is oxidised and dissolved as selenious acid. The beaker is then removed from the hot plate, the clock-glass washed down and the solution diluted to about 25 c.c. If any insoluble residue is present, the solution is filtered, the filtrate and washings being collected in a 250 c.c. beaker; if no insoluble residue is present, the solution is simply transferred to a 250 c.c. beaker. In either case, the excess nitric acid present in the solution is then just neutralised by means of ammonia, after which strong hydrochloric acid is added to give an acidity of at least 1 in 3 by volume of hydrochloric acid (sp. gr. 1·16), the total volume then being about 100 c.c. The selenium is precipitated from this solution in one of the following ways:—

(*a*) The cold solution is saturated with sulphur dioxide and then boiled until the red precipitate becomes brownish-grey and coagulated.

(*b*) The solution is boiled for fifteen minutes with an excess of potassium iodide; or

(*c*) The solution is heated to gentle boiling and, under a clock-glass, a sufficient quantity of 10 per cent. hydrazine hydrate is cautiously added, great care being exercised in this operation to prevent a mechanical loss of selenium during a too rapid evolution of nitrogen. (A tall beaker should be used.) When the separated selenium appears grey and further additions of hydrazine hydrate produce no further precipitate, heating is discontinued.[2]

[1] Meyer, *Z. anal. Chem.*, 1914, **53**, 145.
[2] **For details of a method to eliminate all risk of mechanical loss, see Meyer,** *loc. cit.*

Whichever method of precipitation is used, the selenium is filtered through a Gooch crucible, washed with water and alcohol, dried at 105° and weighed. When sulphur dioxide is used as the precipitant, it is advisable to test the filtrate for completeness of precipitation by means of ammonium sulphite crystals.

Gold is used for the production of ruby glass and is usually added to the glass batch as a solution of gold chloride, more rarely as purple of Cassius. A commercial method is to pour the gold chloride solution on a portion of the sand to be used, dry this off, and then mix with the remainder of the batch.

Decolorising Agents.—Practically all glassmaking materials contain more or less iron oxide, and the molten glass extracts small quantities from the refractory container in which the glass is melted. As a consequence, all glass intended to be colourless has a slight greenish tinge due to the presence of iron oxide unless steps are taken to counteract this colour. The tint caused by iron oxide is neutralised, partly by adding to the batch oxidising materials such as the nitrates of sodium or potassium which oxidise ferrous to ferric oxide, in which state its colouring power is greatly diminished, and partly by adding to the batch small quantities of other colouring agents which produce a colour complementary to that caused by the iron oxide and so neutralise it more or less completely. For the latter purpose, the decoloriser most generally used in pot furnaces is manganese dioxide, frequently in conjunction with a trace of cobalt oxide, especially in the case of soda glasses. For use as a decoloriser a good grade of manganese dioxide is desirable, with as low an iron oxide content as possible, say, below 0·5 per cent. (see p. 163).

Nickel oxide is sometimes used for decolorising, especially with potash glasses. For this purpose a trace of cobalt as impurity in the nickel oxide is not deleterious (see p. 161).

Selenium or sodium selenite is the most widely used decoloriser for tank furnace glasses and is invariably added with a considerable excess of white arsenic (see p. 164).

Prepared Decolorisers.—In recent years a number of patent "decolorisers" have been used to a considerable extent. These usually consist very largely of arsenious oxide together with some or all of the materials mentioned as decolorisers. The most frequently used combination is selenium powder with a little cobalt oxide (often in the form of "powder blue," see p. 161), and from twenty to forty times its weight of arsenious oxide. Antimony oxide is also sometimes added and the authors have examined prepared decolorisers containing, in addition to arsenic, selenium and cobalt, appreciable quantities of manganese, nickel and titanium oxides and calcium carbonate—the last mentioned being merely a diluting agent. The accurate analysis

of such mixtures is exceedingly difficult and is rarely called for, since they are sold as "decoloriser" without any specified composition. They may be examined by removing the volatile constituents (arsenic and selenium) and examining the residue qualitatively. The quantitative determination of the bases is devised according to the nature of those present. Separate determinations must be made for the arsenic and selenium according to the methods indicated on pp. 165 and 168.

F. Miscellaneous Raw Materials

Under this heading are included the oxides of arsenic and antimony, which are used in small quantity for very many glasses, and therefore they usually appear only as minor constituents, though both oxides are occasionally employed as major constituents in the manufacture of optical glass, and antimony oxide occurs in some chemical resistance glasses to the extent of up to 4 per cent.

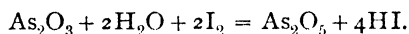
Arsenic trioxide is usually referred to in the glass trade as, simply, "arsenic." It occurs to a large extent in prepared decolorisers, and it is added to batches prepared for the manufacture of glasses when selenium or manganese dioxide is used for decolorising, because it stabilises the action of those materials. "Arsenic" itself, preferably in the presence of potassium nitrate, has a decolorising action, probably due to the formation of a colourless ferric arsenate which reduces the tendency of small amounts of iron oxide present in glass to give a faint greenish tint. In some of the best "crystal" glasses, where brilliancy is a very essential factor, "arsenic" is the only decolorising agent used, and so the slight loss of brilliancy caused by decolorising with manganese dioxide is avoided. "Arsenic" is also sometimes used for stabilising the colour of pale green glasses. Some manufacturers add "arsenic" or antimony oxide to their batches to assist in "plaining" the glass during the melting process, that is, in rendering it free from small air bubbles.

Arsenious Oxide—As_2O_3—white arsenic, or simply "arsenic," is the form in which arsenic is almost invariably used in glassmaking, though very occasionally the element itself is employed and, in special optical glasses, the pentoxide. As arsenious oxide is a volatilised product it may be obtained commercially in a high state of purity and is frequently sold with a guarantee of a minimum content of 99 per cent. As_2O_3. Cornish "arsenic" is usually of this grade, but cheaper grades of Mexican and Japanese "arsenic" are obtainable which contain 95 to 97 per cent. As_2O_3.

The testing of a sample of "arsenic" is comparatively a simple matter since, if pure, it should be completely volatile. If, therefore, a dry sample is gently heated in a porcelain crucible (under a good

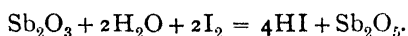
draught hood) until all the volatile matter has been expelled, the loss in weight may be taken to represent As_2O_3. The residue, if any, should be examined for colouring agents, especially the oxides of iron and copper, which would reduce the value of the sample considerably, particularly if intended for use in a flint glass.

A direct determination of the amount of As_2O_3 may be speedily made if desired by dissolving, say, 1 g. of the sample in a solution of sodium hydroxide (10 per cent.), slightly acidifying the solution with hydrochloric acid, adding a saturated solution of sodium bicarbonate containing about 3 g. $NaHCO_3$, and titrating the solution with a standard iodine solution, using starch solution as indicator. The reaction is as follows:—

$$As_2O_3 + 2H_2O + 2I_2 = As_2O_5 + 4HI.$$

The hydriodic acid is neutralised as formed, by the sodium bicarbonate, and the end of the reaction is indicated by the appearance of a faint trace of free iodine,[1] with which the starch solution forms a deep blue colour.

Antimony Compounds.—The antimony compound most frequently used in glass manufacture is the trioxide, Sb_2O_3. It possesses no colouring power except when used in large quantities in heavy lead glasses, when it produces a yellow tint. It is usually used as a fining agent, to assist in freeing the glass from minute air bubbles though its precise action is rather obscure, since it does not appear to volatilise at the founding temperature. If pure, antimony oxide should be completely soluble in a hot solution of tartaric acid and the usual trade specification is its solubility in this reagent. To test a sample, digest say 1 g. of the dried material with a hot strong solution of tartaric acid, with repeated additions of small quantities of the acid until no further solution takes place. Filter off the clear solution, wash the insoluble thoroughly with hot dilute tartaric acid solution and finally with hot water. Dry and ignite the filter paper at a low temperature and weigh. Good samples are usually above 99·5 per cent. soluble.

A direct determination of the antimony may be made in the tartaric acid solution by the above method for arsenic, namely, by adding an excess of sodium bicarbonate solution (*i.e.*, first neutralising with the bicarbonate solution and then adding a further 15 to 20 c.c.), and titrating the resulting solution with standard iodine, using starch as the indicator as described above. The reaction is:—

$$Sb_2O_3 + 2H_2O + 2I_2 = 4HI + Sb_2O_5.$$

1 c.c. of N iodine solution is equivalent to 0·0072 g. Sb_2O_3.

[1] Mellor, *Treatise on Quantitative Inorganic Analysis*, 1913, p. 293. Scott, *Standard Methods of Chemical Analysis*, 1918, p. 35.

Antimony sulphide sometimes occurs in old glass recipes as a colouring agent, but in all probability the colour produced is due to the sulphur alone.

The Determination of Iron Oxide in Glass and Glassmaking Materials

The total amount of iron oxide in glass or glassmaking materials may be determined either (*a*) gravimetrically, (*b*) volumetrically, or (*c*) colorimetrically. The gravimetric method involves, in most cases, a tedious separation from alumina and is very rarely employed. The usual method in a complete analysis is to oxidise all the iron to the ferric state (if necessary), precipitate the iron oxide and alumina together as hydroxides and determine the iron oxide separately in a solution of the bisulphate fusion of this precipitate (see p. 241), the alumina being obtained by difference.

The best method to use for the determination of iron oxide will depend largely upon the quantity present. In colourless or only slightly coloured glasses and the raw materials used in their manufacture—or, in general, with materials containing less than 2 per cent. of Fe_2O_3—when 1 to 2 g. of the sample is used for the analysis, the colorimetric method is the most suitable. If the iron oxide present exceeds 2 per cent., it is advisable to use a volumetric method and determine the iron oxide by means of standard potassium dichromate or permanganate solution.

Though the iron oxide is frequently determined in the "ammonia precipitate" obtained in the usual course of an analysis, where great accuracy is desired it is always better to determine the iron oxide on a separate sample brought into solution in a manner suitable for the purpose, since not only do practically all the reagents used contain traces of iron, but also in the prolonged evaporations to remove silica in general silicate analyses it is impossible entirely to avoid contamination by dust, and a correct blank determination is both difficult and laborious.

Solution of the Material

The various materials used for bringing the sample into suitable solution may be grouped conveniently as follows:—

I. Substances soluble in hydrochloric acid, as, for example, the carbonates of sodium and potassium, limestone and lime *after ignition* (if not pre-ignited, these compounds may give insoluble residues containing appreciable quantities of iron oxide), saltcake, etc., etc. Usually these substances dissolve readily on gentle boiling, but where insoluble residues remain, they should be filtered off, washed, ignited in platinum,

fused with a little sodium carbonate, the melt dissolved in hydrochloric acid and added to the main solution.

When the solution is being prepared for a colorimetric determination, it is advisable to keep the amount of free acid low and therefore the sample should be dissolved in as small a volume as possible followed by dilution to a standard volume when solution is complete.

II. Substances which may most conveniently be decomposed with hydrofluoric and sulphuric acids, as described on p. 225, and the resulting residue dissolved in dilute hydrochloric or sulphuric acid. Such substances include all glasses free from lead and barium, clays, silicate minerals and sands.

When the colorimetric method is to be employed, it is advisable to use hydrochloric instead of sulphuric acid for dissolving the residue left after decomposition with hydrofluoric and sulphuric acids, because hydrochloric acid yields solutions which give better colours with potassium thiocyanate than those obtained when sulphuric acid is used. With some silicate minerals there is occasionally a small insoluble iron-containing residue left after decomposition with hydrofluoric and sulphuric acids,[1] and in exact work that insoluble residue is fused with a little sodium carbonate and the resulting melt dissolved in hydrochloric acid. Should any of the residue still remain insoluble, it is fused with a little potassium bisulphate, followed by solution of the fused mass in hydrochloric acid.

III. Substances which are best dealt with by a combination of the two previous methods, that is, first treated with hydrochloric acid to dissolve as much as possible, then the remaining insoluble residue decomposed with hydrofluoric and sulphuric acids. Examples of this class are glass batches, seashore sands, some limestones rich in shale, etc.

IV. Substances which call for the use of nitric acid as, for example, lead compounds. Red lead may be conveniently dissolved in nitric acid with the aid of hydrogen peroxide.

The treatment of insoluble residues and the desirability of restricting the amount of free acid when nitric acid is the solvent is similar to that described under I.

V. Substances which are best decomposed with hydrofluoric and nitric acids, as described on p. 226, the resulting residues being dissolved in dilute nitric acid. Examples are lead and barium glasses.

As already mentioned, when iron oxide is determined in the "ammonia precipitate" the determination is made on the solution of the cake resulting from fusion (carried out as described on p. 240) with potassium bisulphate or pyrosulphate. It is rarely necessary,

[1] Lundell and Knowles, *J. Amer. Ceram. Soc.*, 1928, 11, 119.

but sometimes recommended, to fuse the whole sample with sodium carbonate to bring it into solution, but when this is done it is necessary to ensure that the sodium carbonate is quite free from iron. Frequently sodium carbonate sold as "purest" for analytical purposes contains some iron in the metallic state, and as this is not equally disseminated throughout the reagent it gives rise to variable results, since the additional iron introduced cannot be adequately compensated for by a blank determination.

The Thiocyanate Colorimetric Determination of Iron

This method depends upon the fact that solutions of ferric salts produce with soluble thiocyanates a red coloration and, if the necessary conditions are observed, the intensity of the colour can be used to determine the amount of iron present. All the iron must, of course, be present in the ferric state, which can readily be assured by boiling the solution with a few drops of concentrated nitric acid or hydrogen peroxide.

The solution in which the iron is to be determined is made up to a convenient volume and an aliquot portion taken. Definite volumes of potassium thiocyanate solution and water are added to bring the total volume to a desired amount. The tint so produced is duplicated in a solution similar in other respects but free from iron, by the gradual addition of an iron solution of known strength. The tints of the solutions may be compared in a colorimeter, such as Weller's[1] or Hillebrand's[2] or, with practice, quite successful results may be attained with Nessler's cylinders if great care is taken to ensure that the Nessler cylinders are exactly paired, both as to thickness of bottom and evenness of internal diameter right to the bottom, *i.e.* with no internal taper towards the bottom of the tube.

Convenient solutions for use are: I. A 10 per cent. solution of pure crystallised potassium thiocyanate. II. A solution containing 0·6303 g. of ferric potassium alum per litre and also 5 c.c. of concentrated sulphuric acid.

The standard iron solution, if preferred, may be made by dissolving pure precipitated ferric oxide in sulphuric acid and diluting until 1 c.c. of the solution contains 0·0001 g. of Fe_2O_3 (the same strength as the solution mentioned above prepared from ferric potassium alum). Iron solutions of this concentration and acidity will keep almost indefinitely. For use in the actual determination this solution should be diluted ten or twenty times, by diluting 10 or 5 c.c. to 100 c.c. with distilled water immediately previous to using. The authors prefer the more

[1] A. Weller, *Ber.*, 1882, 15, 2599.
[2] W. F. Hillebrand, *Bull. U.S. Geol. Survey*, 1910, 422, 34.

dilute solution, which contains 0·000005 g. Fe_2O_3 per c.c. The burette from which the diluted iron solution is run should have a very open scale—say a 5 or 10 c.c. burette graduated in 1/50ths.

Two methods of procedure may be used in the actual titration.

Method A. A blank solution is required as the presence of various acids and salts affects the strength of the colour of ferric thiocyanate solutions; the "blank" solution should (for strict accuracy) be identical in composition with the test solution, except that it should be quite free from iron. For technical analyses, identically equivalent composition is not absolutely necessary for the "blank" solution. For instance, when the iron oxide present in a sample of clay is determined on the bi- or pyro-sulphate fusion of the iron oxide and alumina precipitate, a satisfactory "blank" solution consists of one containing 5 g. per litre of iron-free potash alum. The notes given on p. 174 on the influence of various acids and salts will serve to indicate suitable "blank" solutions in other cases, as well as to indicate the degree of error if pure water is used instead of a prepared "blank" solution.

Five c.c. of the solution under examination is pipetted into one of the Nessler cylinders, then one drop of strong nitric acid, 20 c.c. distilled water (from a burette) and 5 c.c. of the 10 per cent. potassium thiocyanate solution are added, making a total volume of 30 c.c. of liquid in the cylinder. Into the comparison cylinder, 5 c.c. of "blank" solution is pipetted, then one drop of strong nitric acid, 20 c.c. distilled water and 5 c.c. of the thiocyanate solution are added. The contents of both cylinders are well agitated, and then dilute standard iron solution is run from the burette drop by drop, with constant stirring, into the comparison cylinder, an equal quantity of distilled water being added to the test solution and well stirred in the other cylinder. The addition of standard iron solution is continued until the colours in the two cylinders exactly match, and then the volume of iron solution added is noted.

The experiment should be repeated three or four times, and the mean value taken for calculating the iron oxide content of the sample. It is always advisable to reverse the cylinders at successive trials, that is, to use for the test solution in the second instance the cylinder which is used for the comparison tube in the first test. This obviates any slight error due to possible slight differences in the form or colour of the two cylinders.

The ferric thiocyanate colour is slightly affected by hydrolysis in pure solutions, so that it is advisable to work always with solutions of approximately the same iron concentration. In an experiment conducted as above, the titration should be about 2 to 3 c.c. of dilute standard iron solution equivalent to 0·000005 g. iron oxide per c.c., and this produces a colour which is fairly easy to match. If the test

solution as obtained in the analysis is too strong in iron oxide (as indicated by a trial determination) an aliquot portion of it should be diluted with distilled water so that 5 c.c. of the solution so diluted will require a titration of 2½ to 3 c.c. of the standard iron solution to produce an equal colour. If the test solution is very weak in iron oxide, instead of adding 5 c.c. of it and 20 c.c. distilled water to the cylinder, 10, 15 or 20 c.c. of the test solution and 15, 10 or 5 c.c. distilled water respectively may be used.

From the volume of standard iron oxide solution required for comparison, the amount of iron oxide present in the total test solution may readily be computed. With high grade sands, limespars, red leads, etc., it is advisable to work with samples of 2 g. or more.

Method B. Sometimes the test solutions do not give very clear pink colours with the thiocyanate solution, due to the influence of other substances in the solution. Brownish tints are sometimes produced, and it is then very difficult to match exactly the colours of the solutions in the two cylinders. The following variation in the procedure helps to overcome this difficulty, and at the same time it obviates the necessity of preparing a "blank" solution.

Instead of making similar solutions in each of the two cylinders, a suitable volume (say, V c.c.) of the test solution is transferred by means of a pipette to one of the cylinders, then two drops of strong nitric acid, 50—V c.c. of water and 10 c.c. of potassium thiocyanate solution are added in this order and the whole (being 60 c.c. in volume) very thoroughly stirred. Twenty c.c. of this solution is removed by a pipette into the second glass cylinder, leaving 40 c.c. in the first cylinder. Dilute standard iron solution is then added to the 20 c.c. drop by drop from a burette, with constant thorough stirring, until the colours of the solutions in the two cylinders match on looking *down the tubes.* It must be noted that the titration value as obtained by this method must be multiplied by 3 to obtain the volume of standard iron solution corresponding to V c.c. of the test solution. As in Method A, the mean value of three or four concordant results should be taken for calculating the iron oxide present in the sample. The strength of the test solution should be such, or the value of "V" should be so chosen, that about 1·5 c.c. (certainly not less than 1·0 c.c. nor more than 2·0 c.c.) of dilute standard iron solution (1 c.c. = 0·000005 g. Fe_2O_3) is required for the titration.

It should be noted that for the same depth of colour (looking *down* the tube) in the comparison cylinders, the titration is twice as great when Method A is used as it is with Method B, so that in this respect Method A is capable of greater accuracy. On the other hand, in many cases it would be very tedious to prepare a "blank" solution containing all the constituents (except iron) present in the test solution, and in

such cases Method B is very useful, since the colorimetric comparison is made in identical solutions. To investigate the importance of having an accurate "blank" solution for Method A, experiments were made by J. D. Cauwood to determine the influence of various common constituents on the intensity of the ferric thiocyanate colour, and his results indicated that:

(*a*) The addition of one drop of strong nitric acid to the contents of each cylinder in Method A (as detailed in the procedure above) tended to intensify and stabilise the colours. With regard to the presence of nitric acid in test solutions: Using 5 c.c. test solution containing 2 per cent. or less by volume of strong nitric acid and nothing else except iron oxide, the nitric acid was found to have an inappreciable effect on the value of the titration obtained by Method A; for such test solutions, therefore, pure water can be used instead of a prepared "blank" with only small risk of error. With test solutions containing 5 to 10 per cent. by volume of strong nitric acid and only iron oxide in addition, working with 5 c.c. test solution, and using pure water (plus the prescribed one drop of strong nitric acid) instead of a prepared "blank" solution in the comparison cylinder, somewhat high titrations were obtained by Method A, the stronger the nitric acid the greater being the error, the titration averaging of the order of 8 to 10 per cent. high with the solution containing 10 per cent. of nitric acid; with such test solutions, therefore, a prepared "blank" solution is necessary for Method A. Where test solutions are prepared for colorimetric iron determinations by dissolving the sample in nitric acid, the amount of excess acid should be kept down to a minimum to reduce the necessity of preparing an accurate "blank" solution for Method A. (Compare p. 170.)

(*b*) Hydrochloric acid was without effect in strengths up to 10 per cent. by volume in the test solution, when 5 c.c. of the latter was used. When this acid is the only constituent additional to the iron oxide, there is, therefore, no necessity to make a prepared blank for Method A (conducted as prescribed) provided the strength of the hydrochloric acid is kept reasonably low.

(*c*) Sulphuric acid gave results which became progressively lower with increasing concentration of sulphuric acid in the test solution. (Working with 5 c.c. test solution, and using Method A, with pure water as "blank," a 2 per cent. by volume sulphuric acid test solution gave a result about 10 per cent. low, and a 4 per cent. sulphuric acid test solution a result about 14 per cent. low.) Correct results were obtained with Method A when the concentration of the sulphuric acid was approximately the same in each of the solutions in the two cylinders. With Method B, moderate concentrations of sulphuric acid were found to be without influence on the result.

(*d*) Calcium chloride tended to give low results, but with the quantities present in technical analyses of limestone and limespars, the effect of the calcium chloride is fairly small, making the results only 5 per cent. or less too low. In other words, using pure water instead of a prepared "blank" solution for Method A, the error in the determination of iron oxide in a sample of ordinary limestone or limespar (dissolved, after strong ignition, in the minimum practicable quantity of hydrochloric acid) should be less than 5 per cent. (low), and the greater the percentage of iron oxide the less the error.

(*e*) Aluminium sulphate in small quantities made no appreciable difference, but caused high results if present in considerable amount. With alumina contents of ten or twenty times the iron oxide present, no appreciable error occurs with Method A even if alumina is not present in the solution in the comparison cylinder.

To increase the sensitiveness of the colorimetric method[1] for the determination of very small quantities of iron, 30 c.c. of the test solution, 5 c.c. nitric acid and 15 c.c. of a 5 per cent. solution of ammonium thiocyanate are shaken up in a stoppered cylinder with 5 c.c. of a mixture of amyl alcohol and ether in the proportions of 5 : 2. A corresponding blank solution is prepared in the same way. The colour of the amyl alcohol-ferric thiocyanate solution is matched by the gradual addition of standard iron solution to the blank. It is claimed that 0·001 mg. of iron can readily be determined.

The Volumetric Determination of Iron.

If iron oxide is present in the sample under investigation to an extent exceeding 2 per cent., one of the usual volumetric methods should be employed for its determination, the iron being first reduced completely to the ferrous state and subsequently oxidised by means of a standard solution of potassium dichromate or permanganate. Potassium permanganate is generally used when the iron is in sulphuric acid solution—as for instance when the determination is made in a solution prepared from the bisulphate fusion of the ignited "ammonia precipitate" (see p. 241), or on a sample decomposed with hydrofluoric and sulphuric acids. Potassium dichromate solution is generally used when the iron is in hydrochloric acid solution.

The reducing agents most frequently employed to convert all the iron present in the solution into the ferrous state are (*a*) metallic zinc, (*b*) ammonium bisulphite and (*c*) hydrogen sulphide. If zinc is used, the solution is reduced in an Erlenmeyer flask fitted with a Bunsen valve. The acidity of the solution should be about 20 per cent., and care should be taken that none of the zinc remains undissolved; or a Jones' reductor (Vol. II., p. 23) may be used. If ammonium bisulphite is used, an acidity of about 7 per cent. is sufficient. The reduction is complete when a drop of the solution removed with the end of a glass rod gives no immediate coloration with a drop of potassium thiocyanate solution on a spotting plate. If ammonium bisulphite or hydrogen sulphide is employed, the excess of the reducing agent must be removed completely by boiling off the sulphur dioxide or hydrogen sulphide respectively before the titration is attempted. This is rather a tedious operation in either case, but these reagents have the advantage over metallic zinc in that the results obtained are not vitiated by the presence of titanium oxide in the solution under investigation. Should titanium oxide be present (as is very frequently the case with clays and sands) zinc may be used as the reducing agent; but after the reduction is complete a little bismuth oxide should be added to the solution to re-oxidise

[1] H. L. Smith and J. H. Cooke, *Analyst*, 1926, 51, 503.

the titanium, and the excess bismuth oxide and bismuth filtered off from the solution.[1]

After the reduction is complete, the solution is titrated with a standard *N*/50 or *N*/100 solution of potassium permanganate or with a standard *N*/50 or *N*/100 solution of potassium dichromate. For the dichromate titration, a freshly prepared solution of potassium ferricyanide may be used as an external indicator on a spotting plate, in the usual way, or alternatively diphenylamine may be used as an internal indicator.

The diphenylamine indicator for the titration of ferrous iron with potassium dichromate is used as follows: One g. of diphenylamine is dissolved in 100 c.c. strong sulphuric acid, and three drops of this solution are used in each titration. (After some time, this diphenylamine solution goes brown but it does not lose its usefulness.) Another solution is also necessary, namely, one consisting of 150 c.c. phosphoric acid (sp. gr. 1·70) and 150 c.c. sulphuric acid (sp. gr. 1·84) mixed together and diluted with distilled water to 1 litre; 15 c.c. of this solution are used in each titration.

For a determination 20 to 25 c.c. dilute (1 : 4) sulphuric acid, 15 c.c. of the prepared phosphoric acid solution and three drops of the diphenylamine indicator are added to the ferrous salt solution under examination and the solution diluted to a bulk of about 250 c.c. Standard *N*/50 potassium dichromate solution is then added from a burette. Near the end-point the green colour of the solution deepens to a blue-green (or greyish-green in the presence of large amounts of iron), and the end-point is reached when one drop produces an intense violet-blue coloration which does not change on the addition of further dichromate.

The method is applicable to both hydrochloric acid and sulphuric acid solutions of ferrous salts, and while it probably works best with *N*/10 dichromate, quite good results are obtainable with *N*/50 dichromate. The results tend to be slightly high, and a correction of 0·05 c.c. must be made for the oxidation of the diphenylamine. The presence of copper reduces the titre, while the presence of trivalent arsenic increases it, but small quantities of either metal do not make an appreciable difference.[2]

The Determination of Ferrous and Ferric Iron occurring together.—Knecht and Hibbert[3] evolved a method for the determination of iron in solution based on the fact that a ferric salt in acid solution is reduced immediately to the ferrous state in the cold by a solution of titanous chloride. This method eliminates the necessity

[1] See Mellor, *Treatise on Quantitative Inorganic Analysis*, 1913, p. 191.

[2] For further particulars see J. Knap, *J. Amer. Chem. Soc.*, 1924, **46**, 263.

[3] *Ber.*, 1903, **36**, 1551.

of reducing the iron before titration and also affords a means of determining ferrous and ferric iron in the same solution, since the ferrous iron may be determined by potassium permanganate (in the presence of manganous sulphate), and the total iron may be determined in the ferric state by titration with titanous chloride using a drop of potassium thiocyanate solution as indicator, and keeping a current of CO_2 passing into the titration vessels. The method is reliable,[1] but the titanous chloride solution must be kept in a neutral atmosphere.

An interesting method of carrying out the titration of iron solutions without having recourse to an external indicator is that described by Ferguson and Hostetter,[2] in which the end-point of the titration is determined by an electrometric method. Briefly, the method consists in reducing the iron in hydrochloric acid solution to the ferrous state by means of a stannous chloride solution, and then oxidising the excess stannous chloride solution and the ferrous iron with standard dichromate solution, plotting the electromotive force produced against the volume of dichromate solution used. The curve produced shows two inflections, the first upon the completion of the oxidation of the excess stannous chloride and the second where all the iron is converted into the ferric state. The locations of the inflection points are definite and the horizontal distance between them gives the volume of standard dichromate used for the oxidation, from which the amount of iron present in the solution may readily be ascertained. The electromotive force developed is read on a potentiometer, a suitable form being that designed by Roberts[3] (*cf.* Vol. II., p. 25).

The titration is carried out in an Erlenmeyer flask fitted with a special "titrating head" which carries a calomel half-cell and platinum electrode, and also enables the titration to be carried out in an atmosphere of oxygen-free nitrogen or carbon dioxide. The method is particularly interesting in that it allows of ferrous and ferric iron being determined in the same solution, provided no other reducing agents are present. A typical curve for this titration is given by Ferguson and Hostetter.[4] This shows a first inflection at a point corresponding to the oxidation of all the iron present in the ferrous state by the standard dichromate solution. The excess of the dichromate solution and the total iron are then reduced by stannous chloride solution and the reduced solution again oxidised by standard dichromate solution. A second inflection point in the curve indicates the point at which the excess of stannous chloride is oxidised completely, and a third that at which all the iron present is completely converted

[1] Treadwell (Hall), *Analytical Chemistry*, 1919, Vol. II., p. 700.
[2] J. B. Ferguson and J. C. Hostetter, *J. Amer. Ceram. Soc.*, 1919, **2**, 608.
[3] *Ibid.*, 1919, **2**, 1358. [4] *Ibid.*, 1919, **2**, 609.

into the ferric state. The horizontal distance between the two latter points gives the amount of dichromate solution necessary to oxidise the total iron present in the solution from the ferrous to the ferric state. Boric acid does not interfere with the determination, but arsenious oxide interferes with the determination of ferrous iron.

According to Ferguson and Hostetter, the iron in a glass could be rapidly and accurately determined by this method by decomposing the glass with pure hydrofluoric acid in a flask of resistant glass and carrying out the titration in the same flask without filtering off any precipitate formed.

It may be noted that in raw materials or glasses containing barium or lead, a considerable proportion of the iron present may be retained by the barium or lead sulphate precipitates respectively if these are precipitated directly from the main solution of the glass. Such precipitations should, therefore, be avoided in connection with solutions in which the iron oxide is to be determined, and that is why it is recommended that the iron oxide in such materials should be determined on a separate sample in nitric acid solution (see pp. 260 and 261).

Heinrichs[1] determined the ferrous iron content of heat protective glasses as follows. To obtain a solution of the glass without oxidising any of the ferrous iron present during the process of solution, a sample of finely ground glass was weighed out in a platinum dish and dissolved with hydrofluoric and sulphuric acids in an atmosphere of carbon dioxide, the dish being placed in a special lead container heated in an air bath. The resulting solution was titrated in the presence of excess of boric acid[2] with $N/100$ potassium permanganate solution.

An interesting study of the various methods of determining iron oxide in glass sands has been made by Lundell and Knowles.[3] In this study the electrometric titration method, the colorimetric method, the hydrogen sulphide reduction method and a gravimetric method are reviewed.

[1] *Glastechn. Berichte*, 1921, **5**, 154. See also Soule, *J. Amer. Chem. Soc.*, 1928, **50**, 1691.

[2] See Barneby, *Chem. News*, 1916, **113**, 7.

[3] *J. Amer. Ceram. Soc.*, 1928, **11**, 119.

II.—THE COMPOSITION AND DURABILITY OF GLASS

A. The Composition of Glass

The range of composition of commercial glasses is at least as wide as the range of commercial alloys, and just as particular metals are used for giving special properties to alloys, so are particular oxides used for the making of special glasses, and therefore fundamental differences in composition may occur between different types of glass. The following notes briefly indicate the chief groups of commercial glasses and their usual composition.

(a) **Bottle Glass and Window Glass.**—These glasses contain silica, lime and sodium oxide as major constituents, and usually small amounts of alumina, iron oxide and magnesia as minor constituents. In some (certain American bottle glasses, for instance) magnesia may be a major constituent (introduced in part replacement of lime), and in others alumina is present as a major constituent. In coloured bottle glass, colouring agents (see pp. 159-166) are also present, and alumina is sometimes a major constituent of these glasses. In so-called Bohemian glass, the sodium oxide is partly replaced by potassium oxide, and therefore in such glass both occur as major constituents (for example, in the glass of certain soda-water syphon bottles).

The following actual analyses show illustrative compositions of some commercial glasses:—

	I. Window Glass.	II. Colourless Bottle Glass.	III. Colourless Bottle Glass containing Magnesia.	IV. Sulphur-amber Bottle Glass containing Alumina.	V. Dark-green Bottle Glass containing Alumina.	VI. A "Bohemian" Glass.
Silica	73·8	74·2	73·7	72·1	66·5	74·7
Lime	12·3	9·1	6·2	8·0	9·8	7·9
Sodium Oxide	13·4	16·3	16·5	16·8	15·5	8·4
Potassium Oxide	...	...	...	...	...	8·6
Magnesia	}	}	3·2	...	...	}
Alumina	} 0·5	} 0·4	} 0·4	2·8	3·0	} 0·4
Iron Oxide	}	}	}	0·2	2·9	}
Manganese Oxide	...	...	...	...	2·3	...

Glasses II. and III. also contained small amounts of arsenic oxide and traces of selenium and cobalt oxide, while Glass IV. contained a small amount of sulphur.

(b) **Crystal and Semi-Crystal Glass; Coloured and Opal Decorative Glasses.**—The best crystal glass, such as that used for cut glass, consists of silica, lead oxide and potassium oxide, usually with only very small amounts of alumina, iron oxide, arsenic and decoloriser as

minor constituents, but sometimes with small percentages of lime or boric oxide, or both, intentionally added. The lead oxide content of such glasses varies from over 40 to about 30 per cent., while the potassium oxide varies from 8·5 to 15 per cent. and the silica from 47 to 54 per cent.; the more brilliant the glass, the higher the lead oxide content.

Cheaper lead oxide glasses, such as those sometimes used for electric light bulbs and blown tumblers, usually contain about 20 per cent. of lead oxide, and part of the potassium oxide is sometimes replaced by sodium oxide. In still cheaper glasses (often called "semi-crystal") the lead oxide is partly replaced by lime, and the potassium oxide partly by sodium oxide; in such glasses, therefore, the major constituents are silica, lead oxide, lime, and potassium and sodium oxides. (It may here be mentioned that many pressed glass articles, designed to imitate cut glass, are made from simple silica-lime-soda glasses of the bottle glass type, while others are made from glasses similar to "semi-crystal," but containing barium oxide instead of lead oxide.)

Coloured or opal decorative glasses, such as those used for fancy vases, globes, etc., are similar in composition to colourless crystal or semi-crystal glasses (according to the quality of the glass), and in addition they contain appropriate colouring or opacifying agents or both (see colouring agents, p. 159, and opacifying agents, p. 153).

(c) **Chemical and Heat Resisting Glasses.**—These are frequently very complex in character, and great variation in composition may exist between equally satisfactory glasses. The best glasses of this class are all of the boro-silicate type, with comparatively low alkali oxide content. Other major constituents which may be present are alumina, zinc oxide, magnesia and lime, the two former occurring more frequently than the two latter. The following analyses show the compositions of six glasses which have been employed for making satisfactory chemical ware, while I. is also used for making oven ware.

	I.	II.	III.	IV.	V.	VI.
Silica	80·6	68·0	66·4	71·0	72·3	66·5
Boric Oxide	11·9	5·8	7·0	7·4	12·6	4·6
Alumina	2·0	2·6	6·5	1·6	4·3	6·7
Zinc Oxide	...	7·4	8·7	5·3	3·4	3·6
Lime	0·2	0·7	0·3	0·5	0·5	4·3
Magnesia	0·1	3·4	0·1	2·6	0·1	0·3
Sodium Oxide	4·1	11·2	10·3	10·7	5·0	11·4
Potassium Oxide	0·3	0·3	0·6	0·3	1·5	2·4
Arsenic Oxide	0·65	...	...	...	...	...
Antimony Oxide	...	0·42	...	0·4	...	...
Iron Oxide	0·15	0·18	0·12	0·2	0·15	0·1
Manganese Oxide	...	Tr.	Tr.	Tr.	0·1	0·1

Boro-silicate glasses of a type similar to some of those in the above table are used for such articles as miners' lamp glasses, searchlight lenses, etc., which require heat resisting glasses.

(d) **Optical Glass.**—The composition of glasses used for lenses, prisms, etc., in optical instruments varies extensively. All the common glassmaking oxides are used in some optical glass or other, the particular oxides employed for any one glass being selected according to the optical properties (refractive index, dispersion, etc.) which they give to the glass. The acidic oxides which may occur in optical glass are silica, boric oxide, and phosphoric oxide, while the basic oxides present may be only one or as many as six or seven of the oxides of sodium, potassium, lead, aluminium, zinc, calcium, barium, and magnesium. With such a complicated series of glasses, it is not possible to quote analyses which are, in any real sense, fully typical, but the following analyses show the composition of some actual optical glasses of different types :—

	I.	II.	III.	IV.	V.	VI.
Silica	70·7	1·0	69·2	20·8	51 7	...
Boric Oxide	...	52 5	2·0	...	...	3·0
Phosphoric Oxide . .	...	...	...	...	...	70·5
Sodium Oxide . . .	2·0	1·5	8·0	...	1·5	...
Potassium Oxide . .	16·0	1·5	11·0	...	9·5	12·0
Alumina	...	9·0	...	...	...	10·0
Lead Oxide	...	16·0	2·0	79·0	10·0	...
Lime	11·0	...	4·0	...	...	...
Barium Oxide . . .	...	12·0	...	...	20·0	...
Zinc Oxide	...	6·0	3·5	...	7·0	...
Magnesia	...	...	...	...	...	4·0
Arsenic Oxide . . .	0·3	0·5	0·3	0·2	0·3	0·5

In the introductory portion of the description of the analysis of glass, further reference is made to the composition of glasses, and the particular uses of certain special constituents are mentioned. The composition of coloured glasses is indicated in the discussion of colouring agents on pp. 159-166.

B. The Durability of Glass

With perhaps the single exception of water glass, the foremost quality which commercial glass should possess is durability, that is, the power of resisting weathering and the action of water and such substances as may come in contact with the glass during normal usage. Expressed in an alternative way, durability can be defined as the power of preserving unaltered over a long period the surface and transparency of the glass without tarnishing or disintegration.

The degree of durability which a commercial glass must possess to make it suitable for its particular purpose depends upon the type considered. The following notes give a brief indication of the resistant properties which glass should exhibit under different conditions of use.[1]

Window glass, both sheet and plate, is often exposed to the attack of wind and rain, and this means not only to the solvent attack of water, carbon dioxide, and other impurities in the atmosphere, but also to the frictional effect of dust particles; the glass used must, therefore, be durable under these conditions.

Bottles, and glass containers generally, should not be attacked or affected by atmospheric moisture, etc., during storage. (Attack by atmospheric conditions is usually referred to as "weathering.") They should be able to withstand commercial washing and sterilising processes without attack or partial disintegration, and to resist the solvent action of contents which might be stored in them. Cases have been met with where milk bottles suffered "spalling" (partial disintegration) during modern, high-temperature sterilisation processes, because the bottles were not made of durable glass. As further examples of the deleterious effect of glass of low durability may be instanced (*a*) in one case, solutions of hydrogen peroxide and (*b*) in another case, a solution of a delicate drug (medicine), which were quite spoiled by alkali oxide dissolved from the glass of the bottles containing them; with bottles made of glass of satisfactory durability, this deterioration would not happen.

Glass insulators must not be liable to attack by moisture, since the visible effect of such attack is preceded by an absorption of moisture in the glass surface which diminishes the insulating power. Decorative and illuminating glass ware must be resistant to water and to "weathering." Boiler gauge glasses must withstand the action of water and steam at high temperatures and pressures.

The durability of chemical and laboratory glassware is of the utmost importance. Reagent bottles must be made of durable glass, otherwise liquid and deliquescent solid reagents will attack the glass and become contaminated with the products of decomposition. No ordinary glass bottles are immune from attack through prolonged contact with strong alkali solutions, and analysts should bear this in mind (see below). Weighing-bottles should be made of durable glass, because a film of moisture (depending as to magnitude on the humidity of the atmosphere) condenses on the surface of glasses which are attacked by water. Beakers, flasks and other analytical apparatus must be durable under the conditions in which they are used, otherwise analytical results might be entirely vitiated owing to contamination

[1] See Cauwood, English and Turner, *J. Soc. Glass Tech.*, 1917, 1, 156.

of precipitates, etc., with the products of decomposition of the glass; for instance, flasks used for wash-bottles should be resistant to boiling water, and beakers used for the determination of silica in steel should be resistant to boiling hydrochloric acid. (At the present time, chemical glassware of excellent durability is obtainable, but even so the use of platinum and silica ware instead of glassware is preferred for such accurate work as atomic weight determinations.[1]) Gases as well as liquids may attack glass surfaces, and a modified surface can have a decided effect upon chemical reactions taking place in its vicinity.[2] Absorption of gases on glass surfaces can occur, and this factor has to be taken into consideration in all very accurate work with gases in glass.[3] As a final example of the necessity of durability in glassware used in the laboratory, it might be mentioned that microscope glass slides should be made of a glass which obviates the risk of microscopic objects mounted between them undergoing changes due to the instability of the glass.[4]

Optical glass must be durable as regards resistance to "weathering," because it is essential that lenses and prisms shall preserve their bright surface after polishing in order to function satisfactorily. Where the desired optical properties of a glass do not permit a composition which confers high durability, such a glass has to be protected by covering it with a more durable lens or cover glass.

Factors affecting the Degree of Attack on Glass.—The chief factors are (1) the nature of the corroding agent, that is, whether the agent is moisture or a particular chemical reagent; (2) the temperature at which the attack takes place; (3) the length of time of the attack; (4) the nature of the glass surface; and (5) the composition of the glass.

1. *Effect of the Nature of the Corroding Agent.* Much work has been carried out to determine the degree of attack on glass of water, of acids, of alkalis and of solutions of salts. Under suitable conditions, hydrofluoric acid will dissolve all glasses, and therefore this acid is never considered in connection with the durability of glass.

In general, it may be said that pure water attacks glasses of good and reasonable durability to a somewhat greater extent than solutions of neutral salts or nitric, sulphuric, acetic and oxalic acids. Hydrochloric acid is more selective in its attack than the four acids mentioned, but the quantitative corrosion produced by this acid is of the same order as that produced by water on glasses of this type, while alkaline

[1] See *Proc. Chem. Soc.*, 1904, **20**, 2; and Richards, *Memoir of the Carnegie Institution*, Washington, 1910, No. 125.

[2] See, for example, Bone and Wheeler, *J. Chem. Soc.*, 1902, **81**, 358.

[3] See "The Weight of a Normal Litre of Hydrogen Chloride," *Trans. Faraday Soc.*, 1911, **7**, 4.

[4] Weber, *Ber.*, 1892, **25**, 2374.

solutions attack such glasses much more strongly than either water or acids. This general statement is illustrated by the following table showing the percentage losses in weight suffered by a number of glasses (in powder form) when boiled for one hour in water and the reagents stated :—

Glass.	Percentage Losses in Weight.			
	Water.	20·24 per cent. Hydrochloric Acid.	2 *N* Sodium Carbonate.	2 *N* Sodium Hydroxide.
A	0·27	0·18	1·8	1·9
B	0·17	0·11	1·3	1·3
C	0·34	0·39	2·1	3·3
D	0·16	0·26	2·0	3·3
E	0·03	0·11	0·25	1·6
F	0·02	0·06	0·3	2·2

It will be seen that for any one glass the attack by the alkaline solutions is greater than by water and hydrochloric acid, that the 2 *N* sodium hydroxide solution causes at least as great and usually a greater loss than the 2 *N* sodium carbonate solution, but that the order of the loss of weight to water and hydrochloric acid depends upon the particular glass. Glass A is a bottle glass of reasonable, and B a bottle glass of good durability, and it will be seen that water attacks these glasses more than 20·24 per cent. hydrochloric acid. Glass C is a soda-lead glass of reasonable durability, D is a soda-lead glass of good durability, while E and F are good zinc-alumina-boro-silicate chemical glasses; in these four glasses, the attack by 20·24 per cent. hydrochloric acid is greater than that by water.[1]

Reagent bottles should be made of glass of durability at least equivalent to that of Glass B, and it will be noticed that with such glass the resistance to water and hydrochloric acid is quite good, but on the other hand the attack by strong alkaline solutions is quite appreciable. This is quite parallel with the repeatedly observed facts that deposits (which are decomposition products of the glass) form at the bottom of strong sodium hydroxide solutions stored for an appreciable time in reagent bottles, whereas no deposits form in the case of acids stored in a similar manner. The storage of strong alkaline solutions in glass should be avoided as much as possible, and strong standard alkali solutions should preferably be freshly prepared just before use. It will also be noticed from the above table that even good chemical ware (E and F) is appreciably attacked by boiling 2 *N* sodium hydroxide.

[1] The figures in the above table and many others of great interest are to be found in a paper by Dimbleby and Turner, *J. Soc. Glass Tech.*, 1926, **10**, 304.

While alkaline solutions usually attack glass more than water and acids, and losses in weight caused by water and hydrochloric acid are of the same order, these statements hold good only for glasses of reasonable and good durability, and not for glasses of poor durability; with the latter glasses water usually gives a much greater attack than hydrochloric acid, 2 *N* sodium carbonate solution a greater attack than 2 *N* caustic soda, and the attack by water may even be greater than the attack by 2 *N* sodium carbonate. This is illustrated by the following figures for percentage losses in weight caused by boiling (powdered) glass for one hour in water and the reagents stated:—

Glass.	Percentage Losses in Weight.			
	Water.	20·24 per cent. Hydrochloric Acid.	2 *N* Sodium Carbonate.	2 *N* Sodium Hydroxide.
798*a*	49·6	5·2	45·6	6·2
798*i*	0·3	0·3	2·2	2·1

Both 798*a* and 798*i*[1] are soda-baryta-silica glasses, the "*a*" glass being a non-durable one and the "*i*" glass durable, and it is seen that the order of the attack by water and the test reagents employed is quite different with the non-durable glass from that with the durable one. While it has been considered advisable to draw attention to this fact, it should be pointed out that the durable glasses are the important ones commercially, and therefore when considering the corrosive effect of different reagents, most stress should be given to the behaviour of those reagents towards durable glasses.

With alkaline reagents the attack on durable glasses increases with increasing strength of reagent. In published results[2] for tests on nineteen chemical glasses, it is found that the loss in weight caused by the attack of 2 *N* sodium hydroxide for three hours at 100° averaged about 4·5 times the loss in weight caused by *N*/10 sodium hydroxide under similar conditions. With acids and neutral salts, the attack on durable glasses varies but little with strength of reagent; with sulphuric acid, for instance, there is little difference between the attack of the concentrated acid and the 2 *N* solution.[3]

2. *The Effect of Temperature.* The higher the temperature, the greater the attack on glass by water and chemical reagents. As an example of this, the following figures for the losses in weight caused

[1] Dimbleby and Turner, *loc. cit.*

[2] Cauwood, English and Turner, *J. Soc. Glass Tech.*, 1917, **1**, 153; and Cauwood and Turner, *J. Soc. Glass Tech.*, 1918, **2**, 219.

[3] Cauwood, English and Turner, *loc. cit.*

by the action of 2 *N* sodium hydroxide for three hours at different temperatures might be quoted:—

Action of 2 N *Sodium Hydroxide at Different Temperatures* *

Losses (of flasks) in mg. per sq. dcm. after three hours' action.

Temperature.	Glass D.	Glass F.	Glass H.
20°	Inappreciable	Inappreciable	...
40°	1·7	1·5	...
60°	4·1	4·3	...
80°	18·9	19·2	24·1
90°	31·7	36·5	45·5
100°	74·2	88·9	154·0

* Way, Cauwood and Turner, *J. Soc. Glass Tech.*, 1917, **1**, 144.

Increasing corrosion with increasing temperature is common to all reagents, but the rate at which the attack increases with rise in temperature varies with different reagents, the rate of increase being less with hydrochloric acid than with water and alkalis. These facts are illustrated by the following results of tests with flasks of Glass F:—

Action of Water, Acid and Alkali at Different Temperatures

Temperature.	Amounts dissolved in mg.		
	Water.	20·24 per cent. Hydrochloric Acid.	2 *N* Sodium Carbonate.
60°	...	...	3·2
80°	...	...	10·6
90°	1·4	5·4	18·1
95°	2·4	7·2	...
100°	5·0	9·3	34·8
102°	...	10·4	...
104·8°	...	12·9	...

The times of the periods during which attack occurred in the above tests were as follows:—With water, twenty-four hours per period; with hydrochloric acid, twelve hours; and with 2 *N* sodium carbonate, three hours.[1] The attack by water gives the loss found in 250 c.c. flasks. The HCl and Na_2CO_3 tests refer to 500 c.c. flasks.

Investigations have also been made of the attack of both water and steam on glass at different temperatures (above 100°) and pressures in the autoclave. W. L. Baillie[2] carried out tests with water at 30 lbs. pressure (121°), 60 lbs. (144°), and 90 lbs. (159°) and found that, generally speaking, the amount of alkali oxide dissolved from the

[1] Cauwood and Turner, *J. Soc. Glass Tech.*, 1918, **2**, 260.
[2] *J. Soc. Glass Tech.*, 1922, **6**, 279.

test glasses employed increased with increasing temperature and pressure. F. W. Hodkin and W. E. S. Turner[1] found, however, that the amounts of alkali oxide dissolved from cast discs of soda-lime-silica glasses by water during autoclave tests were irregular at pressures higher than 5 atmospheres; for instance, in the case of one glass, the alkali extracted was 0·087 g. per 100 sq. cm. at 10 atmospheres and only 0·072 g. at 15 atmospheres. This abnormal result of the smaller extraction of alkali at the higher temperature is attributed by Hodkin and Turner to the formation, at the higher temperatures and pressures of their tests, of a hard crust, probably of hydrated silicate, which retards further action or at least makes that action irregular. On the other hand, F. Friedrichs[2] has reported results of tests with saturated steam for three hours in the autoclave on twenty-two chemical glasses, and those results show a steady increase in both loss in weight and alkali oxide extracted, with increase in temperature, for temperature ranges varying from 150° to 250° for some glasses and from 250° to 330° and even higher with others (tests being made at increments of 10°). It would appear, therefore, that the degree of aqueous attack on glass at temperatures above 100° depends upon whether or not a protective scale is formed on the glass, and where no such scale is formed, the higher the temperature the greater the attack.

3. *The Effect of Time and of Repeated Treatment.* The effect of time on corrosion has not been so extensively studied as some of the other factors. Comparing the extent of corrosion in a short period with that in a long period, it is found that the latter corrosion is the greater, but under certain conditions of test the relation between corrosion and time is not linear. Referring to the attack of water at 100° on alkali-lime-silicate glasses in powder form, Dr M. Thomas[3] stated: "In ordinary glasses the durability appears to improve quickly as the period of treatment is extended. In good glasses this improvement occurs early, but in poor glasses after a longer time. For example, with a medium quality Thuringian glass 75 per cent. of the material extracted in an indefinitely long time is dissolved out in five hours. At the beginning of the test, the proportion of alkalis dissolved out is excessive, but as the period of treatment is prolonged the other constituents (silica and alkaline earths) are dissolved. This corresponds with the generally accepted view that (during attack by water) at first a hydration and hydrolysis of the dissolved silicates takes place and then the alkaline solution so formed attacks the remaining framework of more insoluble substances." This tendency, reported by Thomas, of alkali-lime-silicate glasses to improve in

[1] *J. Soc. Glass Tech.*, 1922, 6, 291.
[2] *Sprechsaal*, 1928, 61, 282.
[3] *J. Soc. Glass Tech.*, 1928, 12, *Proceedings*, p. 87.

durability upon prolonged treatment with water at 100° is parallel with the results obtained by repeated treatments of such glasses with boiling water (see below).

Direct information as to the effect of time on (*a*) the attack of water on complex glasses of the chemical resistance type, and (*b*) the attack of hydrochloric acid and alkaline solutions on glass generally, is not yet available, but indirect evidence can be obtained from published results of the repeated action of water and chemical reagents on glasses of different types. J. D. Cauwood and W. E. S. Turner[1] tested the effect of the repeated action of boiling and evaporating water, boiling and evaporating hydrochloric acid, and of 2 *N* sodium hydroxide and 2 *N* sodium carbonate at 100° on flasks made of different glasses. Their results may be summarised as follows:—

(*a*) Water. In each test, 300 c.c. water was boiled and evaporated to 100 c.c. in two hours, and the test on each flask was repeated ten times successively. With a soda-lime-silica glass (H), almost regular improvement of durability was found with repeated treatments with water, the aggregate loss in weight for the last three tests being only 37 per cent. of the aggregate loss during the first three. With a zinc-aluminium boro-silicate glass (D) and an aluminium boro-silicate glass (F) the results were more irregular, but on the whole they tended to show some improvement in durability with repeated treatments; in each case, the aggregate loss in weight during the last five tests was about 75 per cent. of the aggregate loss during the first five.

(*b*) 20·24 per cent. hydrochloric acid. In each test, 250 c.c. of acid was boiled and evaporated to 100 c.c. in one and a half hours. The soda-lime-silica glass (H) showed regular improvement in durability as the tests proceeded up to twenty-five treatments; the aggregate loss in weight for the first five treatments was 13·0 mg., for the second five treatments, 7·9 mg., for the third five, 5·7 mg., for the fourth five, 3·9 mg., and for the last five treatments, 3·6 mg. On the other hand, two zinc-aluminium-boro-silicate glasses were tested, and the losses in weight per treatment were found to be fairly constant with repeated treatments, one glass (A) being tested fifteen times and the other (D) twenty-five times. Therefore, the durability of zinc-aluminium-boro-silicate glasses is apparently not affected beneficially by continued or repeated treatment with hydrochloric acid.

(*c*) 2 *N* sodium hydroxide. The loss in weight caused by the action of 150 c.c. of the reagent during three hours at 100° was measured, each flask being tested ten times successively. The results tended to show neither increased nor decreased resistance as a result of repeated action on a soda-lime-silica glass (H), a zinc-aluminium-boro-silicate (D) and an aluminium-boro-silicate (F).

[1] *J. Soc. Glass Tech.*, 1918, 2, 235.

(*d*) 2 *N* sodium carbonate. The loss in weight due to the action of 100 c.c. of this reagent for three hours at 100° was measured, each flask being tested fifteen times successively. As with sodium hydroxide, neither increased nor decreased resistance to the action of sodium carbonate solution was found upon repeated treatments, the glasses tested being a soda-lime-silicate glass (H), a zinc-aluminium-boro-silicate (E), and an aluminium-boro-silicate (F). The losses in weight for individual treatments were fairly regular with E and F, but distinctly irregular with H.

4. *Effect of the State of the Glass Surface.* Dealing with physical considerations first, the following points are to be noted:—

(*a*) Surfaces which are abraded or which have been made matt by mechanical means (such as grinding) are more attacked than polished surfaces of the same glass. Ground and incompletely polished test-plates have been found to give greater losses in weight due to corrosion than fully polished plates.[1] Also polished surfaces differ in reactivity from fractured faces.[2]

(*b*) Manufacturing processes can produce conditions in glass surfaces which affect durability. With cast slabs, Hodkin and Turner[3] found differences between the attack on surfaces which had been chilled by the mould and those (the upper ones) which had not, and they further found that under certain conditions excessive attack occurred along the pouring lines. Other observers have noted differences in durability between pressed, rolled, and blown surfaces of the same glass, and V. Dimbleby[4] has stated that the inner surface of a bottle is less durable than the outer which is chilled by the mould during manufacture.

(*c*) Differences in durability occur between annealed and unannealed (or strained) samples of the same glass. This point has been investigated by H. Lober[5] and G. von Keppeler.[6] The former found that annealed flasks were more durable against the action of water than unannealed ones. Except in one test with specially manufactured flasks, Keppeler also found annealed glass more durable against the action of water than unannealed, tests being made both with powdered glass and with flasks.

Durability can also be influenced by a number of factors which affect the chemical state of a glass surface. Reference has already been made (see p. 188) to the fact that certain glass surfaces which

[1] Turner, *J. Soc. Glass Tech.*, 1922, **6**, 39.

[2] Jackson and Haigh, *Report of the Brit. Sci. Instrument Research Association*, 1921, on the "Durability of Optical Glasses."

[3] Hodkin and Turner, *J. Soc. Glass Tech.*, 1922, **6**, 291; see also Adams, *ibid.*, 1922, **6**, 304; Dimbleby and Turner, *ibid.*, 1926, **10**, 313; and A. E. Williams, *J. Amer. Ceram. Soc.*, 1922, **5**, 504.

[4] *Glass*, 1926, **3**, 61.

[5] *Sprechsaal*, 1928, **61**, 160.

[6] *Ibid.*, 1928, **61**, 300.

have been continuously treated with water or with dilute acids are more durable to those liquids than fresh unused surfaces. Further, G. Gehlhoff and R. Schmidt[1] have observed that annealed glass plates having a fire-polished surface give up less alkali to water than plates of the same glass which have been ground and mechanically polished, while Lober[2] and Keppeler[3] have independently observed that annealing and re-annealing in open type lehrs (that is, in contact with the furnace gases with their charge of carbon dioxide, sulphur dioxide and water vapour) give a surface more durable to water than is obtained when the same operations are carried out in closed lehrs (where the glass articles do not come in contact with the furnace gases). These improvements in durability are believed to be due to the removal of some alkali oxide from the glass surfaces by the treatments mentioned.

All the above factors have to be taken into consideration when selecting samples and tests for durability determinations.

5. *The Relation between Composition and Durability.*—The durability of a glass, as glass, depends upon both the nature of the actual components and their relative proportions. Various methods have been used in attempts to measure the durability of glasses, but as the simplest, and the one of most general applicability, we may consider the solubility of the various glasses in water and in acid and alkaline solutions.

Effect of Basic Constituents.—The simplest glass is one composed of two components only, namely, sodium oxide and silica. It has been shown by Peddle[4] that the solubility of such glasses in powder form in water at 80° depends upon the relative proportions of soda and silica contained. Under the test conditions employed by Peddle, glasses containing 28 per cent. of soda and upwards are completely soluble, but the solubility decreases rapidly with decreasing sodium oxide content, being 74·71 per cent. with a glass containing 23·66 per cent. of sodium oxide, and 31·92 per cent. with one containing 17·13 per cent. soda. These results were confirmed by Dimbleby and Turner,[5] and indicate that a simple silica-soda glass would have no practical utility on account of its solubility. (The water-glass of commerce is a strong solution of sodium silicate in water.)

If, however, a portion of the sodium oxide is replaced by an $R^{ii}O$, $R^{iii}_2O_3$ or $R^{iv}O_2$ oxide the durability of the resulting glass is materially improved, and this the more, the greater the amount of the $R^{ii}O$ ($R^{iii}_2O_3$, $R^{iv}O_2$) base substituted for sodium oxide within the limits of technical glass manufacture. In the commoner types of glass, such as are used for the production of bottles and jars, sheet and plate glass,

[1] *Sprechsaal*, 1926, **60**, 338. [2] *Ibid.*, 1928, **61**, 160. [3] *Ibid.*, 1928, **61**, 300.
[4] Peddle, *J. Soc. Glass Tech.*, 1920, **4**, 14.
[5] Dimbleby and Turner, *J. Soc. Glass Tech.*, 1926, **10**, 314.

etc., the $R^{II}O$ base almost always used is lime, both on technical and economic grounds, though other bases are also used for particular purposes, such as the oxides of lead, barium, magnesium, zinc and aluminium.

The effect of the progressive substitution of sodium oxide by the bases named (and also by titania and zirconia) in glasses of the general molecular type $(2-x)\ Na_2O : x R^{II}O : 6\ SiO_2$ was studied by Dimbleby and Turner.[1] The results are given in a series of tables and graphs and indicate very clearly the improvement effected in the durability of the soda-silica glasses by the gradual substitution of other bases for part of the soda. In this work, the substitution was carried out on a molecular basis. This was preferred to a percentage basis since the problem is not one concerned with mixtures of oxides only, but deals with compounds, partly dissociated, in the presence of excess of another constituent (silica). In the soda-lime-silica glasses, the difference between comparison on a molecular and a percentage basis is not very marked since the molecular weights of soda (62) and lime (56) are fairly close, so that the substitution of one for the other does not influence the percentage of silica present to any great degree, and it remains in the region 74 to 75 per cent. If the effect of the substitution of soda by lime is considered on a molecular basis and the effect of the other oxides compared on similar lines, the relative molecular effect of the different bases will be arrived at.

(*a*) Lime. Starting with the standard trisilicate soda glass and substituting lime for soda in gradually increasing proportions, keeping the glass of the general composition $(2-x)Na_2O : x\,CaO : 6\ SiO_2$, it was observed that the addition of lime in small quantities greatly improved the durability of the glass and that the improvement was progressive with increasing proportions of lime. The following table[2] shows the attack by water, acid and alkaline solutions on glasses of this nature:—

Glass No.	Per cent. CaO.	$\frac{\text{Mols. } Na_2O}{\text{Mols. CaO}}$	Loss in Weight in			
			Water.	HCl.	$2N.\ Na_2CO_3$.	$2N.$ NaOH.
2	1·50	14·44	17·68	...	...	...
3	2·61	8·00	2·78	1·70	8·00	2·59
4	3·81	5·13	1·40	0·51	8·60	2·42
5	4·50	3·99	0·60	0·37	2·67	2·19
7	7·45	2·00	0·27	0·18	1·78	1·90
9	9·36	1·38	0·22	0·13	1·50	1·48
10	10·38	1·18	0·17	0·11	1·31	1·26
11	11·68	0·97	0·17	0·10	1·26	1·20

[1] Dimbleby and Turner, *J. Soc. Glass Tech.*, 1926, **10**, 316.
[2] Dimbleby and Turner, *loc. cit.*, 348.

It is evident from the above table that when the soda and lime are present in approximately equimolecular proportions very durable glasses are obtained on a tri-silicate basis whether the attack is by water, acid, or alkaline solutions.

(*b*) Barium Oxide. The substitution of soda by barium oxide in molecular proportions is attended by a similar improvement in the durability of the glasses produced, though not quite as much as with lime.

(*c*) Lead Oxide. Similar to lime and barium oxide, but rather more effective than lime.

(*d*) Magnesia. Similar to the preceding oxides but rather more effective than lead oxide.

(*e*) Zinc Oxide. Zinc oxide has the best influence on durability of all the $R^{ii}O$ oxides.

(*f*) Alumina. Alumina is one of the most effective oxides in promoting durability in glass, but it cannot be added to the ordinary series of tri-silicate glasses to the same extent as the $R^{ii}O$ bases on account of the difficulty in melting the resulting glasses.

(*g*) Iron Oxide.[1] The molecular substitution of this oxide for soda gives improved durability towards attack by boiling water and boiling sodium carbonate to a degree very similar to that obtained with alumina. As regards resistance to hydrochloric acid, however, iron oxide is not so effective as alumina (on a molecular basis), while the progressive substitution of iron oxide for soda in tri-silicate glasses leads to progressively *decreased* resistance to caustic soda (but nevertheless all the iron-oxide glasses examined are more resistant to caustic soda than the $2\,Na_2O\,.\,6\,SiO_2$ glass, and the earlier members of the iron oxide series more resistant than the molecularly corresponding titania, lead oxide, barium oxide and zinc oxide glasses).

(*h*) Zirconia and Titania. Both these oxides exert a markedly beneficial effect on durability whether added in substitution for soda or silica in the tri-silicate glasses.

The durability of the tri-silicate glasses is, therefore, increased by the molecular substitution of some of the soda by the oxides mentioned above. Omitting iron oxide from discussion, owing to the anomalous results regarding resistance to caustic soda of glasses containing iron oxide, the greatest improvement in durability is effected by zirconia, the other oxides following in the order of alumina, titania, zinc oxide, magnesia, lead oxide, lime and baryta.

The following table[2] shows the attack of boiling water, acid and alkaline solutions on glasses of the general molecular formula

[1] Dimbleby and Turner, *J. Soc. Glass Tech.*, 1928, **12**, 52.

[2] Compiled from Dimbleby and Turner, *J. Soc. Glass Tech.*, 1926, **10**, 348-355.

$(2-x)\ Na_2O : x\,RO : 6\,SiO_2$. The results have been selected as far as possible to show the durability of glasses in which half the soda has been substituted molecularly by another oxide; but this was not always possible (as melting difficulties prevented the preparation of the glasses) and, therefore, to enable comparison to be made of the effect of the different oxides, the ratio $\frac{\text{Molecules of Soda}}{\text{Molecules of RO}}$ is shown in the third column.

Type of Glass.	Percentage $RO(R_2O_3, RO_2)$.	$\frac{\text{Mols. } Na_2O}{\text{Mols. RO.}}$	Percentage Loss in Weight in			
			Water.	HCl.	$2N.\ Na_2CO_3$.	$2N.$ NaOH.
Baryta glass, No. 798*j*	26·25	1·05	0·20	0·25	1·90	1·60
Lime „ „ 11	11·68	0·97	0·17	0·10	1·26	1·20
Magnesia „ „ 389	8·45	1·00	0·12	0·10	1·90	2·09
Zinc „ „ 788*i*	13·07	1·00	0·11	0·11	0·20	1·94
Iron „ „ 814*j*	26·35	ca 1	0·09	0·30	0·43	3·97
Titania „ „ 754*k*	14·91	1·00	0·08	0·14	0·70	2·76
Lead „ „ 804*h*	27·77	1·60	0·16	0·26	1·98	3·27
Alumina „ „ 446	12·69	1·50	0·17	0·18	0·38	2·62
Zirconia „ „ 748*h*	10·33	3·00	0·19	0·54	0·45	0·69

It will be seen that the glasses for which this ratio is approximately unity in the above table are correctly arranged as regards resistance to boiling water, but they are not in their correct order as regards resistance to acid and alkalis. Thus, different oxides can exercise beneficial effects on durability in different directions; for instance, zirconia appears to give the best resistance to caustic soda, while lime, magnesia and zinc oxide give the best resistance to hydrochloric acid in the $Na_2O : R^{II}O : 6\,SiO_2$ glasses.

In all the foregoing cases the alkali oxide under consideration has been sodium oxide. If potassium oxide be used instead of sodium oxide the results follow on parallel lines, though generally the molecular substitution of potash for soda leads to increased solubility of the resultant glass. This is indicated in tables given by Peddle,[1] which show that in alkali-lime glasses of similar molecular composition the potash glasses are more soluble than the soda glasses. Another interesting feature in these glasses is that when potash and soda are used together in equimolecular proportions the solubility values obtained are intermediate between those for soda and potash separately, except in the case of glasses $100\,SiO_2 : 10\,Na_2O : 10\,K_2O : 5\,CaO$ and $100\,SiO_2 : 10\,Na_2O : 10\,K_2O : 10\,CaO$ which are less soluble than either of the corresponding soda or potash glasses, the figures being as follows,

[1] Peddle, *J. Soc. Glass Tech.*, 1920, 4, 95.

the solubility being expressed in milligrams dissolved per 100 g. of glass.

x = mole of CaO.	Series 100 SiO_2 : 20 Na_2O : x CaO Solubility.	Series 100 SiO_2 : 10 Na_2O . 10 K_2O : x CaO Solubility.	Series 100 SiO_2 20 K_2O : x CaO Solubility.
5	1915	1658	5145
10	845	784	1384
15	419	547	927
20	253	330	581
30	217	219	342
40	157	196	291

In the case of alkali-lead glasses Peddle[1] found that if the alkali content is greater than 20 per cent. by weight, the potash glasses were more soluble than the soda glasses, but where the alkali content was less than 15 per cent. the soda glasses were the more soluble; and that substituting silica for alkali (*i.e.*, increasing the acidity of the glass) was as valuable a means of improving the durability of the glass as substituting lead oxide for alkali. Keeping the percentage of alkali constant, the durability of the glass can be improved by using a mixture of soda and potash instead of either separately. Peddle[2] states: "In the alkali-$R^{II}O$-SiO_2 glasses, when the total alkali present is less than 20 per cent., the glass containing both alkalies in equal proportion by weight will be less soluble and more durable than either the glass containing all its alkali as potassium oxide or all its alkali as sodium oxide. This is true whatever the percentage of RO or SiO_2 in the glass." RO may be represented by CaO, PbO, BaO, MgO, ZnO, SrO.

The Effect of Acidic Constituents—(1) Silica. In a general way, it can be said that silica tends to promote good resistance to attack by water and acids but not to attack by alkaline solutions.

(2) Boric Oxide. The effect of the gradual substitution of part of the silica by boric oxide in standard glasses of the type $(80-x)$ per cent. SiO_2 : x per cent. B_2O_3 : 20 per cent. Na_2O and of $(90-x)$ per cent. SiO_2 : x per cent. B_2O_3 : 10 per cent. Na_2O has been studied by Dimbleby and Turner,[3] who found that in the series containing 10 per cent. soda the replacement of silica by boric oxide did not result in any increase in the chemical durability of the glasses so produced. In the series containing 20 per cent. soda, it was found that the substitution of some of the silica by boric oxide increased the durability within a limited range. Thus, up to a boric oxide content of from 8 to 11 per cent. the durability increased, but above this limit it decreased slowly up to

[1] Peddle, *J. Soc. Glass Tech.*, 1920, **4**, 353.
[2] Peddle, *J. Soc. Glass Tech.*, 1921, **5**, 196.
[3] *J. Soc. Glass Tech.*, 1926, **10**, 327.

about 15 per cent. boric oxide and very rapidly afterwards. The glasses containing over 15 per cent. boric oxide are attacked by water, hydrochloric acid, 2 *N* sodium hydroxide and 2 *N* sodium carbonate, and the ready solution of the boric oxide from the glasses in all the reagents named indicates that it can only be held very loosely in combination, and that the compound is readily decomposed.

In another investigation by Turner and Winks,[1] a similar conclusion as to the effect of boric oxide was obtained. They substituted boric oxide for silica, stage by stage, in a glass corresponding to Kavalier's chemical glass, having the percentage composition SiO_2—75·82, B_2O_3—nil, Al_2O_3—0·59, Fe_2O_3—0·07, CaO—8·56, Na_2O—6·86, K_2O—7·90, and from their results it is obvious that, in glasses of this type at any rate, the substitution of silica by boric oxide is of practically no advantage as far as chemical durability is concerned, and beyond a limited stage is actually detrimental.

The best types of chemically resistant glass contain boric oxide on account of its great effect on the thermal endurance of the glass, but their durability is usually due to their comparatively low alkali and high RO or R_2O_3 content, alumina and zinc oxide being specially valuable additions.

(3) Phosphoric Oxide. Some glasses have been made containing phosphoric oxide or phosphoric and boric oxides as the acidic part of the glass in place of silica. These glasses were intended for special optical purposes, and are not suitable for general use on account of their lack of durability. According to Zschimmer[2] they are all hygroscopic.

Determination of the Durability of Glass

From time to time various methods have been employed for testing the durability of glass. Weber[3] attempted to arrive at comparative results by exposing glasses to the action of hydrochloric acid vapour and afterwards to air. Mylius[4] tested the action of hot water on powdered glass and also introduced the action of iodo-eosin on a glass surface as a comparative test. The artificial weathering of a glass surface on exposure to pure moist air for a definite period was used by Zschimmer.[5] An interesting method of determining the attack of water on glass vessels was to place pure water in contact with the vessel and determine the increase in its electrical conductivity after a definite time.[6] A test that could be very generally applied was to

[1] *J. Soc. Glass Tech.*, 1926, **10**, 102.
[2] E. Zschimmer, *Chem. Zeit.*, 1901, **25**, 69.
[3] R. Weber, *Dingler's Polyt. Jour.*, 1863, **171**, 129; *Ann. Phys. Chem.*, 1879, **6**, 43.
[4] F. Mylius, *Z. Instrumentenkunde*, 1888, **8**, 267; *Z. anorg. Chem.*, 1907, **55**, 233; *ibid.*, 1910, **67**, 200.
[5] Zschimmer, *Z. Elektrochem*, 1905, **11**, 629.
[6] Kohlrausch, *Ber.*, 1891, **24**, 3560. Haber and Schwenke, *Z. Elektrochem*, 1904, **10**, 143.

expose the glass in the form of rod to the action of superheated steam for a definite period at a definite temperature and pressure in a sealed tube,[1] or to heat in an autoclave a vessel made of the glass and containing water.[2] A general method, which could be applied equally well to solutions as to water, was to allow the test liquid to stand, or be boiled, in contact with a definite area of the glass surface for a specified time and to determine the degree of attack either (*a*) from the loss in weight of the vessel, (*b*) by evaporating the solution and determining the amount of the residue, (*c*) by determining the alkalinity of the solution, (*d*) by complete analysis of the solution, or (*e*) by using more than one of these processes conjointly.[3]

From 1914 to 1918, many new resistant glasses were placed on the market and the testing and comparison of these glasses was carried on with great activity. The effect of water and acid and alkaline solutions on beakers and flasks was very thoroughly investigated and the results published in detail.[4] A considerable amount of work was also done with regard to the solubility of glasses in powder form and also in respect to "weathering," chiefly in connection with optical glasses.[5] Schott and Gen. in certain catalogues arranged glasses in five classes tabulated under the headings h^1 to h^5 according to their respective durabilities. The test was seven days' exposure of a freshly fractured surface to an atmosphere saturated with moisture at 18°, iodo-eosin being used as the indicator. The results were calculated in terms of milligrams of alkali extracted per square metre, and the grades were as follows:—

h^1	0-5	milligrams	of alkali	extracted	per square metre
h^2	5-10	"	"	"	"
h^3	10-20	"	"	"	"
h^4	20-40	"	"	"	"
h^5	over 40	"	"	"	"

Peddle confirmed the conformity of these classifications with the actual weathering results of the glasses in use and also with tests done on powdered glass samples.

When using the powdered glass test, it was found that the fineness of the powder had a very considerable effect on the results obtained. Thus, Nicolardot[6] found that the attack by hydrochloric acid increased

[1] F. Foerster, *Z. anal. Chem.*, 1894, **33**, 304, 386.

[2] Lesure, *J. Pharm. Chem.*, 1910, **1**, 66.

[3] E. C. Sullivan, *J. Soc. Chem. Ind.*, 1916, **35**, 513. P. Nicolardot, *Compt. rend.*, 1916, **163**, 335.

[4] P. Nicolardot, *Compt. rend.*, 1916, **163**, 355. Cauwood, English and Turner, *J. Soc. Glass Tech.*, 1917, **1**, 153.

[5] Peddle, *J. Soc. Glass Tech.*, 1920, **4**, 14, 36, 55, 67, 93, 307, 327, 351. Von Bichowsky, *J. Amer. Ceram. Soc.*, 1920, **3**, 296.

[6] P. Nicolardot, *Compt. rend.*, 1919, **169**, 335.

rapidly with increasing fineness of powder, but that the attack by water was not so much affected. Most powdered glasses were attacked to a greater extent by hydrochloric acid than by water, the opposite being the case when whole glass surfaces, *e.g.* beakers or flasks, were used for the test. In powdered glass tests, therefore, it was very necessary to adhere to a very well-defined grade of powder or the results obtained might be misleading.

Since the war period, the development of the testing of the durability of glasses has been extended considerably, not only in connection with chemically resistant glasses but also in regard to glasses used for containers, such as bottles and jars, the use and production of which has grown very greatly during the last decade. The chief researches dealing with this question will be referred to when dealing with the methods of testing recommended below.

Though many attempts have been made, no series of tests has as yet been generally accepted as "standard," but the movement towards the specification of standard tests for glassware is very persistent, and a series of generally accepted standard tests is expected in the near future. The tests described and referred to below are amongst those most suitable and generally accepted for testing the durability of glasses for general and particular purposes.

Tests of Durability

1. **On Powdered Glass.**—The method of treating powdered glass with certain reagents under prescribed conditions probably gives the best comparative results for glass as glass, although tests done on certain vessels—say flasks or beakers—give valuable information regarding the utility of glasses for special purposes. In the latter case, however, the results obtained are not of general application since they deal principally with a glass surface, and the properties of surface layers frequently differ appreciably from those of the glass as a whole.

In testing glasses by the powder method, it is highly essential that the samples should be uniform, so as to present, as nearly as possible, equal surface areas per test sample to the action of the reagent. By using glass in powder form, a very large surface compared with the weight of glass used is exposed to attack. A suitable grain size for tests is from 20 to 30 mesh, that is, glass powdered so that it passes completely through a 20-mesh standard sieve of the Institute of Mining and Metallurgy, and is retained completely on a 30-mesh sieve. The glass sample should be examined microscopically and all needle-shaped fragments rejected. All glass dust (produced during the crushing of the sample) must be removed from the surface of the grains, as otherwise an increased surface area would be exposed to attack. This may be carried out by washing with cold water on the finer sieve, followed

by washing with a little absolute alcohol, after which the sample is dried and weighed.

The actual test consists in boiling 10 g. of the prepared sample in 500 c.c. of the specified reagent, the volume of the reagent being kept constant during the test. A convenient method of carrying out the test is to suspend the weighed powder in the solution in a platinum gauze bag of about 90-mesh.[1] This avoids the bumping so generally met with when the powder is placed on the bottom of the boiling vessel and also facilitates the removal of the powder after the treatment. Dimbleby and Turner[2] weighed out their test samples in a platinum gauze bag and then thoroughly washed the grains in the bag with absolute alcohol until constancy of weight was obtained. The gauze bag, therefore, was distinctly useful in affording easy manipulation for removing all dust from the test grains.

The reagents usually employed for testing durability by this method are boiling water, boiling 20·24 per cent. hydrochloric acid, boiling 2 *N* sodium hydroxide and boiling 2 *N* sodium carbonate, the time of attack being one hour. A silica beaker may be used as the reagent container for the water and acid tests, in which case the trouble due to bumping when treating samples not in a gauze bag is reduced. A silica basin, through which cold water is circulated, placed on top of the beaker, forms a suitable condenser[3] to prevent evaporation losses during test. A silver beaker may conveniently be used for the alkali tests.

After a test treatment, the solid residue may be collected, washed, dried, and weighed in a Gooch crucible, or, if a gauze bag has been used, simply washed, dried and weighed in the bag. Frequently the solution contains fine flakes, resulting from the decomposition of the glass, and these should be separated from the glass grains as far as possible and included with the liquid, since they are really a result of the attack. If a gauze bag is used, the flakes are found mainly in the liquid outside, but the residual glass grains should be washed free from flakes.

The amount of attack on a sample may be evaluated (1) by determining the loss in weight, (2) by evaporating to dryness in a platinum basin the solutions obtained in the case of water and hydrochloric acid tests, and weighing the residues after gentle ignition and (3) by determining the amount of total alkali extracted in the case of water tests. Useful additional information can be obtained from the appearance of the glass grains after treatment.

Dimbleby and Turner[4] suggested certain standards from the results of their experiments with glass powders, carried out as above. Thus for good bottle glasses they gave the maximum permissible loss in

[1] Dimbleby and Turner, *J. Soc. Glass Tech.*, 1926, **10**, 307. [2] Dimbleby and Turner, *loc. cit.*
[3] See Cauwood, Clarke, Muirhead, and Turner, *J. Soc. Glass Tech.*, 1919, **6**, 228.
[4] Dimbleby and Turner, *J. Soc. Glass Tech.*, 1926, **10**, 345.

boiling water to be 0·27 per cent., the alkali extracted from the glass 0·15 per cent., the loss in hydrochloric acid 0·17 per cent. and in the 2 *N* alkaline solutions 2·0 per cent. Above these limits, bottle glasses could not be regarded as satisfactory. For chemically resistant glasses, the suggested standards were as follows. With boiling water not more than 0·1 per cent. loss, while the alkali extracted should not exceed 0·01 per cent.; with hydrochloric acid, 0·12 per cent. maximum loss; with 2 *N* sodium carbonate, 0·4 per cent. and 2 *N* sodium hydroxide, 2·0 to 3·0 per cent. maximum losses. An exception may be made in regard to certain glasses with high silica and boric oxide content which give very good results with the water and hydrochloric acid tests but fail to resist caustic alkali. Such glasses must undoubtedly be classified as first class chemically-resistant glasses for general use, but cannot be recommended for use with caustic alkali solutions. For glasses for lamp-working purposes, the recommendations were that in the test with boiling water the limits should be 0·3 per cent. total loss in weight and 0·1 per cent alkali extracted. For a really good lamp-working glass, these limits should be reduced to 0·2 per cent. and 0·075 per cent. respectively.

It has not, as yet, been possible to fix standards for all types of glass, but comparative tests can always be made. Thus, irrespective of the actual absolute figures obtained in the tests, it is always possible to compare a certain glass with a corresponding glass known from experience to be of good quality, and thus to arrive at an estimate of the probable durability of the glass in question.

An interesting critical survey of the determination of the durability of glasses by the powder method is given by Thomas,[1] in which the effect of the grain size of the samples, the amount of the sample used, the temperature and the duration of the treatment are considered. A distinction is made between surface and deep-seated durability, the former being dependent upon the action of the test liquid upon the surface of the glass grains, and the latter being largely influenced by the reaction between the products of solution in the case of surface attack and the residual framework of less soluble substances. If surface attack be the chief object of the study, the size of sample treated should be comparatively large, the duration of the treatment fairly short, and smaller grain sizes may be used. If the investigation is concerned chiefly with deep-seated durability, the sample should be as small as possible consistent with obtaining a residue, after evaporation of the solution, sufficiently large to permit of analysis; the grain size should be large and the duration of the test extended. In either case, it is important that the grain size should be even, that is, that the ratio of maximum to minimum grain size in the sample should

[1] *J. Soc. Glass Tech.*, 1928, 12, Proc. 87.

be as nearly 1 : 1 as possible. For practical reasons it is not possible to reduce this ratio below a certain figure. The proposed standard method for testing the durability of glasses by the powder-grain method suggested by the No. 1 Committee of the Deutsche Glastechnische Gesellschaft is as follows.[1] A volume of glass corresponding to 10 g. of a glass of specific gravity 2·5 and grain size 0·3 to 0·49 mm. is leached with water for five hours at a temperature of 100°.

With this quantity of glass and this size of grain, the method is applicable even to good glasses which dissolve only to a slight extent. The period of five hours has been found to be long enough to effect the solution of nearly all the material that would be extracted in a prolonged time, and the temperature of 100° is selected as being easily maintained. It is desirable that the water should be kept in brisk movement by the boiling.

2. **Autoclave Tests.**—What is most generally required from durability tests is information as to the actual corrosion of articles under customary conditions of use. With any reasonably good types of glass (excluding certain optical glasses) the time required to produce a sufficiently definite result under such conditions is too long to permit of such a test being carried out as a general procedure, and it is therefore desirable to accelerate the attack on the glass during tests. To avoid a prolonged series of tests using different reagents, a single reagent, usually water, is selected as being the most suitable corrodent, though this course is not free from objection.[2] On general grounds, the single test for durability recommended by Baillie[3] is to heat the samples *in steam* in an autoclave, the temperature, pressure and the duration of the treatment being selected to suit the particular type of glass under investigation. Autoclave tests have the advantage of being flexible, and require little accessory apparatus. It is very necessary to choose conditions suitable to the type of glass tested. Thus, water vapour at 80° will indicate differences in optical glasses,[4] but it would hardly affect good types of apparatus glass even in thirty hours.

The conditions of test recommended as most suitable for different types of glass by Baillie and Wilson[5] are as follows:—

Resistance quality apparatus glass . . .	3 hours	at 90	lbs./sq. in.
Superior blown ware	3 „	50	„
Softer blown ware	2 „	30	„
Bottles for ordinary laboratory purposes . .	2 „	30	„

[1] M. Thomas, *J. Soc. Glass Tech.*, 1928, **12**, Proc. 104.
[2] Cauwood, English and Turner, *J. Soc. Glass Tech.*, 1917, **1**, 153.
[3] *J. Soc. Glass Tech.*, 1922, **6**, 279.
[4] Elsden, Roberts and Jones, *J. Soc. Glass Tech.*, 1919, **3**, 52.
[5] Baillie and Wilson, *J. Soc. Chem. Ind.*, 1922, **41**, 50 T.

When possible, finished articles should be used as test pieces, since polished surfaces do not react in the same way as fractured faces. Where finished articles are not available, suitable test pieces may be cut and the edges allowed to weather for a few days in a dust-free atmosphere before the test is carried out. Samples are prepared for test by washing successively with 5 per cent. cold acetic acid, water, absolute alcohol and ether, drying for fifteen minutes at 50°, and cooling in a desiccator. They are subsequently handled only by means of platinum-tipped tongs.

The procedure employed by Baillie and Wilson was as follows. The weighed and measured test pieces of 3 to 4 sq. dm. surface were placed on copper gauze in a silica beaker covered by a suitably perforated cap. The beaker stood on a perforated brass plate on a tripod of such height that the plate was just above the level of the water in the bottom of the autoclave. A litre of ammonia-free water was used. The head of the autoclave was finally screwed down at 100°, as this was found to prevent leaks developing later, and after steam had blown off freely for a short time (to displace the air in the autoclave) the valves were closed. The temperature was then increased to attain the desired pressure in a standard time (fifty minutes for the 90 lb. pressure tests), and after holding at that pressure for the test period (two or three hours, according to the glass being tested), steam was immediately blown off. When the temperature fell to 30°, the test pieces were removed from the autoclave and, after cooling under a bell-jar, washed well with ammonia-free distilled water, the washings being collected in a 250 c.c. silica flask and made up to the mark. An aliquot portion of this solution was removed, after thorough shaking, evaporated to dryness with a few drops of sulphuric acid, ignited for three minutes at 600°, cooled and weighed. The remainder of the solution was used for volumetric determinations of the alkali liberated by the steam attack, using iodo-eosin as indicator and *N*/500 sulphuric acid, although for severe attack it may be necessary to use *N*/50 or *N*/20 acid, and methyl red as indicator. The titrations were carried out in 250 c.c. silica flasks, and 20 c.c. of ethereal iodo-eosin (5 mg. per litre) was added as indicator for the *N*/500 acid titrations, cold solutions being used to prevent evaporation of ether.

Using the above procedure, Baillie and Wilson found that results of the alkalinity titrations gave good indications as to the durability of the test samples, but that the weights of the sulphated residues gave much less decisive information. The "total alkalinity," as determined by such titrations, is not due to alkalis alone; but, nevertheless, it is a useful criterion of durability, and the results can conveniently be expressed as mg. of sodium oxide. Baillie and Wilson suggest the

following classification based on "total alkalinity" determinations after three hours at 90 lb. per sq. in.:—

(*a*) For "Resistance" glass—alkalinity should not exceed 0·3 mg. Na_2O per sq. dm.
(*b*) For "Durable" glass—alkalinity 0·3 to 0·8 mg.
(*c*) For "Less durable" glass—alkalinity 0·8 to 2·0 mg.
(*d*) Unsuitable for laboratory use—alkalinity exceeding 2 mg. Na_2O per sq. dm.

Superficial deterioration and loss in weight caused by autoclave tests can be judged by inspection and weighing, after drying the test pieces (from which the soluble decomposition products have been washed) for one hour at 100° and cooling in a desiccator over sulphuric acid. The appearance of the sample after test is frequently of use in judging durability, but apparently the change in weight is the least useful criterion from which to draw conclusions, unless the loss is quite appreciable.

Some glasses after testing in an autoclave may be covered with gelatinous or flaky material which partly scales off on drying. This scale should be removed and determined separately, since it yields soluble alkali compounds and, therefore, affects both the alkalinity determination and the "residue on evaporation." The removal of the scale is difficult to carry out successfully, but according to Baillie[1] it may be accomplished by drying at 100°, followed by prolonged desiccation over sulphuric acid *in vacuo*, after which the scale can be removed by a camel hair brush. To avoid this lengthy procedure, the amount of removable matter may be determined by subjecting the dried and weighed test pieces to the abrasive action of wet, graded sea-sand, after which they are again dried and weighed. To determine how much of the loss is due to abrasion, a blank test is carried out on a test piece of similar size and shape which has previously been tested in the autoclave and cleaned in this manner, and it is claimed that if the procedure is carefully standardised, the method, while not of the highest accuracy, gives reasonably good results. It should be noted that if the surface of a test piece is knocked, increased action, sometimes amounting to "pitting," may occur at the particular points during an autoclave test (*cf.* p. 189).

An autoclave test procedure for chemical ware recommended by the Glass Research Committee of the Institute of Chemistry,[2] and generally approved by the National Physical Laboratory, was as follows:—Distilled water is heated to boiling point in the vessel to be tested, which is then rinsed and the water poured out. The vessel is then rinsed out with a little 5 per cent. acetic acid and some pieces

[1] W. L. Baillie, *J. Soc. Glass Tech.*, 1922, 6, 282. [2] *J. Inst. Chem.*, 1920, 3, 202.

of filter paper, and finally cleaned with hot distilled water. After cleaning in this manner, the vessel is filled with distilled water and placed in an autoclave containing water, being supported *above the surface of the water* on a flat silver plate and surrounded by a silver cylinder which is covered by another silver plate. The heating is conducted for three hours at a registered pressure of 60 lb. per sq. in. After cooling, half the water in the vessel is evaporated to dryness in a weighed platinum dish, the residue heated for one hour at 120°, gently ignited (three minutes at not more than 640°) and weighed. The area of the interior surface of the vessel is calculated and the results expressed in mg. per sq. dm. The alkalinity of the remaining half of the liquid is determined by titration with $N/10$ or $N/100$ sulphuric acid using, say, bromothymol blue as the indicator, and the result expressed as c.c. $N/100$ acid per sq. dm. of surface. The appearance of the glass is noted when dry. The standards suggested for good glasses were a maximum of 4 mg. per sq. dm. for the residue and of 5 c.c. $N/100$ sulphuric acid per sq. dm. for the alkalinity. The surface of the vessel after drying should not show signs of flaking or peeling.

It will be noted that, whereas in Baillie and Wilson's method the test piece is subjected to the action of steam, the attack is by water in the above procedure. By selecting suitable pressures and periods of exposure, similar procedures can be usefully employed for all types of container and laboratory glass.

Withey[1] pointed out that the relative classification of different glasses based on autoclave tests could vary considerably with the duration of the test and the pressure employed. With certain types of glass, protective coatings are formed under certain test conditions, and these coatings can exert a marked effect on the result. Hodkin and Turner[2] also noted the formation of protective coatings on certain soda-lime-silica glasses which they used in a series of autoclave tests up to twenty-five atmospheres. These observations indicate the necessity for employing only carefully selected conditions for autoclave tests, but provided that the conditions are properly selected for the type of glass under examination, an autoclave test is probably the best single test of durability, particularly of finished articles as distinct from glass as glass. For determining the durability of boiler gauge glasses and the like, autoclave tests are undoubtedly most suitable.[3]

3. **Tests for Bottles and Containers.**—During the past ten years much more attention has been paid to the durability of bottles and

[1] W. H. Withey, *J. Soc. Glass Tech.*, 1922, **6**, 289.

[2] Hodkin and Turner, *J. Soc. Glass Tech.*, 1922, **6**, 291.

[3] See Baillie, *J. Soc. Glass Tech.*, 1922, **6**, 279, for arguments in favour of the autoclave test and for references.

containers, and in consequence many tests for these articles have been devised and employed. As the most important durability considerations for bottles and containers are resistance to weathering and to the attack of aqueous solutions stored in them, it is customary to determine their durability by some type of water test. The principal tests are as follows:—

Qualitative Tests. (a) *Boiling Test.* A useful test suggested by A. E. Williams[1] is to suspend the sample or samples in distilled water in a closed vessel with a small steam vent. The water is heated to boiling and boiled for six hours, precautions being taken to ensure that the samples are completely covered with boiling water throughout the test period. After this boiling treatment, articles of good glass show no signs of corrosion, scumming or pitting, whereas articles of non-durable glass show signs of attack—the less the durability the greater the corrosion.

This test is very suitable and fairly adequate for determining the durability of glass bottles, containers, pressed tumblers, etc. Care, however, must be exercised in the selection of samples for test, and articles which have been scratched, abraded or chipped should not be used, as they show corrosion at such places even if the glass is quite durable.

(b) *Narcotine Hydrochloride Test.* A procedure which has been found to be satisfactory[2] for bottles is as follows. The test bottle is cleaned by successive washings with 5 per cent. acetic acid, distilled water and alcohol, and then dried. The bottle is next suspended in a water-bath with the mouth just above the level of the water, which is heated to boiling. When that stage is reached, 50 c.c. of 0·1 per cent. narcotine hydrochloride solution, freshly prepared and heated to boiling in platinum or good resistance glass, is poured into the bottle, which is then closed with a plug of cotton wool. The bottle remains suspended in the boiling water and is examined from time to time, its durability being judged as follows:—

1. If the liquid in the bottle becomes cloudy within ten minutes, the glass is unsatisfactory.
2. If cloudiness appears after ten minutes and gradually increases, the glass is of moderate durability, but not sufficiently good to contain medical preparations.
3. If after fifteen to twenty minutes, minute needles appear but do not increase to any large extent in an hour, the glass is of satisfactory durability.
4. When the liquid is unaltered for one hour, the glass is of excellent durability.

[1] A. E. Williams, *Glass Industry*, 1922, 3, 47.
[2] See Blackmore, Dimbleby and Turner, *J. Soc. Glass Tech.*, 1923, 7, 122.

The above test, while of general applicability, is eminently suitable for medicine bottles, since medicines frequently contain salts of the alkaloids which are sensitive to the influence of even traces of alkali extracted from glass. It should be noted, however, that with this test small bottles may show a worse result than large ones made of the same glass, because with the former there is a comparatively greater surface of glass exposed to attack; comparative tests should, therefore, be made with bottles of the same size.

Quantitative Tests are carried out by determining the total alkali extracted by water at 100° or in an autoclave under pressure.

Dimbleby and Turner[1] have worked out details of a test at 100° along lines first investigated by Palmer,[2] and their procedure is as follows. For maintaining the bottles at 100° during the test period, steam heating is employed. For this purpose, a water-bath about 18 in. deep and about 12 in. diameter is recommended. About 7 in. depth of water is placed in the bath at the commencement of a test, and the test bottles are suspended in a wire cage just above the boiling water. The bottles are surrounded by a metal jacket having a light lid fitted with a sleeve or hole for a thermometer. This jacket is preferably about 9 in. deep, of such diameter as to give about 1½ in. clearance between the jacket and the boiler wall, and it is best suspended so that the top of the jacket is 1 in. or so below the rim of the boiler.

Six bottles are taken for test from the batch to be tested. The samples are thoroughly washed out several times with tap water, then three times with $N/10$ acetic acid, draining well before each washing. All traces of acetic acid are removed by four washings with distilled water, with a one-minute draining period after each wash, and finally the samples are rinsed and warmed to at least 50° with successive small quantities of hot carbon dioxide-free distilled water, care being taken not to crack the bottles. After emptying out the final rinsings, the warm bottles are filled to the base of the neck with boiling CO_2-free water and covered with copper capsules made by folding copper discs to fit the mouths of the bottles. The distilled water used for the test should be boiled in flasks made of best resistance glass, and an ample supply of it should be available to ensure expeditious filling of the samples. Meanwhile the water in the bath should be raised to boiling, and the filled bottles at once put in the wire cage, which is then immediately placed in position in the water-bath and inside the metal jacket, the lid of which is then put on and a standardised thermometer, fitted with a cork, inserted through it, the burner being removed from under the water-bath while these operations are proceeding. The time is then noted, the burner is replaced and the water in the bath

[1] Dimbleby and Turner, private communication.
[2] L. A. Palmer, *J. Amer. Ceram. Soc.*, 1923, 6, 579.

brought rapidly to the boil, after which the gas flame is regulated until ebullition is not too violent but sufficient to give a continuous escape of steam between the lid and the bath. (Seven inches of water will boil gently and keep the temperature constant for six hours without renewal, but very slow boiling gives low results.) After heating the bottles in this manner for six hours, they are removed from the bath, the contents of each bottle poured and drained into a good quality chemically resistant conical flask, and the alkali extracted from each sample determined by titration. It is recommended that these titrations be carried out by first adding about twice the amount of *N*/100 sulphuric acid required to neutralise the alkali present in each solution, then boiling the solutions for fifteen minutes to expel carbon dioxide and, after adding bromothymol blue (10 drops of a 0·04 per cent. solution in redistilled methylated spirits) as indicator, titrating back the excess acid, while very hot, with freshly standardised *N*/100 sodium hydroxide entirely free from carbonate. The results are calculated as mg. of sodium oxide, and the average of at least four results is taken as representing the average of the batch of bottles tested.

In the above procedure, which has been favourably considered by the Standards Committee of the Society of Glass Technology for adoption as a standard test for the durability of bottles (but with a five-hour test period instead of the six hours mentioned above), heating by steam is preferred to heating by water, because the former method appears to give a more even temperature amongst the different bottles tested at one time. With regard to the results, however, it should be noted that old bottles give indication of a better durability than new ones of the same glass, whether the old ones have been used or not. Since the cleansing process to which the samples are subjected removes the products of any "weathering" which may have taken place, and as "weathering" (or use) removes alkali from the surface glass of bottles which have been "weathered" (or used), such bottles under the above test conditions give up less alkali than newly-made ones (*cf.* p. 189). Hence, newly-made bottles should always be used for comparative or standard tests.

After a test, the samples used should be dried and examined for superficial deterioration, whereby qualitative information concerning the durability of the samples is obtained (as with the "Boiling Test," p. 204).

The procedure for autoclave tests is the same as that described above except that the bottles are heated in an autoclave under pressure instead of in steam at 100°. Autoclave tests have the advantage of taking less time than tests at 100°, and while no specific conditions have yet been accepted as standard, tests are most frequently carried out for two hours at 30 lb. pressure per sq. in.[1]

[1] See p. 200; also W. E. S. Turner, *J. Soc. Glass Tech.*, 1919, 3, 41.

Powder tests and standards of suitable durability for bottle glass have already been described (p. 198), but the tests described in this section indicate the durability of the actual articles tested, which is a desirable feature.

4. **Tests for Chemical or Laboratory Glassware.**—In ordinary use, chemical glassware differs from all other types in that it is subjected to the action of widely differing reagents such as acids, both concentrated and dilute, and caustic or carbonated alkalis, and at temperatures varying from the normal to the boiling points of the reagents, frequently over a considerable period of time. It is evident, therefore, that no single test with one reagent is fully adequate to discriminate between various types of chemical glass. No general type of glass can reasonably be expected to be superior to any other in all respects. If so constituted as to be extremely resistant against acid attack, the glass will usually be found susceptible to the attack of alkaline solutions. In order to arrive at a satisfactory verdict as to the general value of a chemical glass, it is necessary, therefore, to carry out a series of tests and compare the sum of the results.

The earliest reliable published information on the attack of a series of reagents on glassware is that given by F. Foerster.[1] At a later date Walker[2] published the results of tests of the action of a series of reagents upon chemical glassware, and noted a considerable difference between the resistance exhibited by flasks and beakers of the same glass. He was also able to draw a broad distinction between alkali-lime silicate glasses and boro-silicate glasses, the latter being superior.

Comparison between French and German chemical glasses was carried out by Nicolardot,[3] who tested the action of water, ammonia, ammonium chloride, sodium chloride, hydrochloric acid, and also the behaviour of the glasses in the autoclave. The results of Walker and Nicolardot were chiefly comparative, and the exact temperature conditions were not stated.

A thorough investigation into the durability of various British, American and European chemical glasses was carried out by Cauwood, English and Turner,[4] who determined the attack of all the reagents commonly used in analytical processes, and also the attack in an autoclave. As the result of an exhaustive investigation, it was concluded that six tests were adequate to determine definitely the quality of chemical glassware, namely, tests with (1) boiling water; (2) water at 183° (an autoclave test); (3) $2\,N$ sodium hydroxide solution; (4) $N/10$ sodium hydroxide; (5) $2\,N$ sodium carbonate, and

[1] F. Foerster, *Z. anal. Chem.*, 1894, **33**, 381.
[2] P. H. Walker, *J. Amer. Chem. Soc.*, 1905, **27**, 865.
[3] P. Nicolardot, *Compt. rend.*, 1916, **163**, 355.
[4] Cauwood, English and Turner, *J. Soc. Glass Tech.*, 1917, **1**, 153. (See also Cauwood and Turner, *ibid.*, 1918, **2**, 219; Muirhead and Turner, *ibid.*, 1919, **3**, 129.)

(6) constant boiling hydrochloric acid (= 20·24 per cent. HCl), and the procedure employed for these tests was as follows:

The tests were carried out on similar vessels, and new 500 c.c. flasks were found to be the most suitable (Florence flasks with flat bottoms). On account of the very slight losses in weight experienced in many of the tests, it was always considered advisable to use a similar flask as a counterpoise in all weighing operations.

Before being subjected to treatment, the flask (and the counterpoise flask) was thoroughly rinsed out five or six times with distilled water and then allowed to stand overnight filled with distilled water. It was then emptied, rinsed out thoroughly twice with 100 c.c. of $N/10$ acetic acid, again washed out with distilled water and finally rinsed with absolute alcohol, after which it was dried in a steam oven, cooled by drawing a current of air through it and then allowed to stand on the balance pan for ten to fifteen minutes before weighing. The counterpoise flask was subjected to exactly the same cleaning treatment as the test flask *both before and after a test*, and placed on one pan of the balance when the test flask was put on the other.

1. *The Boiling-Water Test.* To determine the action of boiling and evaporating water, the cleaned, weighed flask was charged with 300 c.c. distilled water and heated on an asbestos-covered hot plate, the heat being so adjusted that evaporation of the water took place at an average rate of 50 c.c. each half hour. After two hours' evaporation (*i.e.* when the water was reduced to 100 c.c.) the test was arrested. The action on the glass was estimated (*a*) by determining the loss in weight of the flask after rinsing out and drying, and (*b*) by a determination of the alkalinity of the residual 100 c.c. of water, titrating with $N/100$ acid.

Out of twenty-two types of ware tested, sixteen were classed as "good" with losses in weight varying from 0·5 to 1·4 mg., two with losses of 2·8 and 3·7 mg. respectively were classed as "moderate," and three with losses ranging from 5·5 to 14·4 mg. were classed as "bad."

2. *Water and Steam Attack in the Autoclave.* The test employed was more severe than those quoted on p. 200, and was as follows. The cleaned, weighed flask was charged with 250 c.c. conductivity water and, with its mouth loosely covered with platinum foil, placed on a strip of platinum in an autoclave and there heated for three hours at 183° with a steam pressure of 10 kg. per sq. cm., the time taken to heat up to 183° being forty-five minutes. The amount of attack was evaluated (*a*) by titrating the alkalinity of the water in the flask after the test, and (*b*) by determining the total loss in weight. Useful information was also obtained by inspecting the flasks after test.

The losses in weight suffered by flasks classed as "good" were all less than 100 mg. (actual losses for twelve good types varied from

15·4 to 85·9 mg.), those classed as "moderate" suffered losses from 100 to 200 mg., while those in the "bad" class actually had losses varying from 994 to 4917 mg. It is of interest to note that two glasses classed as "good" by the boiling water test were only "moderate" in the autoclave test, and the "moderates" in the former test were classified "bad" by the latter.

3. *Hydrochloric Acid Test.* The reagent used was constant boiling hydrochloric acid (20·24 per cent.) prepared by mixing two volumes of pure concentrated acid (sp. gr. 1·16) with 1·15 volumes of distilled water. Cleaned and weighed flasks were charged with 250 c.c. acid, and 150 c.c. was evaporated off in one and a half hours (50 c.c. per half hour) in the same manner as in the Boiling Water Test. The amount of attack was estimated (*a*) by determining the loss in weight of each flask, and (*b*) by weighing the residue obtained by evaporating the residual 100 c.c. acid to dryness in a platinum basin, adding a little strong ammonium carbonate solution, evaporating again, and finally igniting the residue very gently (not over 650°) over a small moving flame. (A blank determination should be carried out with the acid and the weight found deducted from the weight of residue noted.)

Each flask was tested three times, and classification was eventually made on the aggregate losses in weight for the three tests. On this basis, types suffering losses of less than 10 mg. (the actual results varied from 0·7 to 9·7 mg.) were classed as "good," those with losses of 10 to 15 mg. were classed "moderate," and where the loss exceeded 15 mg. (two actual results being 18·0 and 31·8 mg.) the durability was classed "bad." It is interesting to note that two glasses which were "good" with the Boiling Water Test were "bad" towards Hydrochloric Acid, thus showing the desirability of testing with various reagents instead of only one.

4. *Tests with 2 N Sodium Hydroxide, 2 N Sodium Carbonate and N/10 Sodium Hydroxide.* In each of these cases, weighed flasks, cleaned as described above, were charged with 150 c.c. of the solution and heated to 100° on a hot plate (this required about ten minutes) and then kept at 100° in a paraffin wax bath for three hours, the mouths of the flasks being closed by rubber stoppers fitted with long glass condensing tubes. The corrosive action of the reagents was estimated by determining the loss in weight of the flasks. When cleaning a test flask from paraffin wax, the counterpoise flask was always treated similarly. The interiors of the test flasks were shaken vigorously with distilled water and filter paper pulp to remove any flakes of solid material, and after drying and weighing, the flasks were inspected for etching and visible signs of corrosion.

Three treatments with the particular reagent employed were given to each test flask, and the aggregate losses in weight per sq. dm.

for the three treatments were calculated and used as the basis of a tentative classification as follows :—

Durability Classification.	Loss in Weight per sq. dm. in Nine Hours with :—		
	2 N Sodium Hydroxide.	N/10 Sodium Hydroxide.	2 N Sodium Carbonate.
Good	Less than 300 mg.	Less than 70 mg.	Less than 100 mg.
Moderate . . .	300-400 ,,	70-100 ,,	100-175 ,,
Bad	Over 400 ,,	Over 100 ,,	Over 175 ,,

The actual results obtained by Professor Turner[1] and his co-workers varied from 235·8 to 470·3 mg. with 2 N sodium hydroxide, 41·0 to 136·8 mg. with N/10 sodium hydroxide, and 74·1 to 600·7 mg. with 2 N sodium carbonate. It is of interest to note that a glass, which was the best as regards durability indicated by the hydrochloric acid and the two water tests, had only "moderate" resistance to alkali according to the above classification, again indicating the value of a series of tests with different reagents.

In carrying out tests with alkaline reagents, temperature control is very important, as the rate of attack is markedly affected by temperature[2] (*cf.* p. 185).

Taking the sum of the results of the six tests outlined above, a reliable indication of the durability of chemical glasses under ordinary laboratory operations is obtained, and while these tests do indicate that very high resistance to water and acid may be obtained at some sacrifice of durability towards alkalis, yet out of twenty-two glasses tested, six were classed as "good" by all tests, showing that a successful compromise composition is possible.

The Glass Research Committee of the Institute of Chemistry[3] recommended standard tests for chemical glassware to include (*a*) an autoclave test as described on p. 202; (*b*) a boiling and evaporating test with hydrochloric acid, the attack being determined by weighing the solid matter (obtained by evaporation) dissolved by the acid; (*c*) a test with a boiling ammoniacal solution of ammonium chloride, the amount of corrosion being determined by evaporating the residual solution to dryness in platinum, gently igniting and weighing the residue; and (*d*) a boiling 2 N sodium hydroxide test, in which the loss in weight is determined to estimate the attack. It will be seen, therefore, that in these tests also, different reagents are employed to estimate the all-round durability of glassware.

[1] Cauwood and Turner, *J. Soc. Glass Tech.*, 1918, 2, 230.

[2] See Way, Cauwood and Turner, *J. Soc, Glass Tech.*, 1917, 1, 145, and Cauwood and Turner, *J. Soc. Glass Tech.*, 1918, 2, 260.

[3] *J. Inst. Chem.*, 1920, 3, 202.

Reference has already been made to the glass powder tests for chemical glassware (see p. 199) and to an autoclave test suggested by Baillie (p. 200).

5. **Tests for Optical Glassware.**—Optical glasses frequently differ greatly from the types of glass used for containers and for laboratory ware in that their constitution is determined to a great extent by the optical constants required (dispersion, refraction, etc.) and consequently durability is a somewhat minor consideration. Indeed, in extreme cases, the susceptibility of some optical glasses to atmospheric attack is so great that optical systems containing them require to be carefully protected from the atmosphere. It will be obvious, therefore, that tests designed to discriminate between the more resistant types of glass are not generally suitable for the investigation of optical glasses.

Optical glasses are not required to resist the action of acid or alkaline solutions, and the most important factor as regards durability is their power to withstand corrosion through the action of dust and moisture in the atmosphere. Further, though the durability of the glass, as glass, may be ascertained from powders,[1] optical glasses in use generally possess a highly polished surface, and as the nature of the surface affects the degree of attack to a considerable extent, tests on optical glasses are usually carried out on polished specimens.

Zschimmer[2] published observations on the decomposition of about 200 pieces of glass with plain polished surfaces when exposed to air and dust over a period of several years. Such a test, however, is too lengthy for general use, and the following are the tests usually employed.

The Iodo-Eosin Test. If a glass surface is brought into contact with a solution of iodo-eosin in aqueous ether, water is absorbed by the glass and alkali liberated. The alkali is coloured red by the iodo-eosin and the depth of the coloration is a measure of the attack on the glass. This method of testing durability was used by Mylius[3] and has been followed by later investigators. Elsden, Roberts and Jones[4] tested both a freshly broken surface of the glass and a similar surface after "weathering" for seven days in moist air at 18°. The method for the estimation of the alkalinity by the iodo-eosin reaction recommended in the Report of the Scientific Instrument Research Association (1921) is as follows:—

The iodo-eosin solution is prepared by shaking up ether and distilled water at the ordinary temperature until the ether is saturated. The aqueous ether is then removed and iodo-eosin dissolved in it to the extent of 1 g. per litre. The surface of the glass is immersed

[1] See Peddle, *J. Soc. Glass Tech.*, 1920, 4, 39.
[2] *Chem. Zeit.*, 1901, 25, No. 69.
[3] *Silikat-Zeitschrift*, 1913, 1, 2, 25, 45.
[4] *J. Soc. Glass Tech.*, 1919, 3, 55.

for one minute in the ethereal iodo-eosin solution, and the coloured film produced removed by a few c.c. of a 0·1 per cent. solution of sodium carbonate into one tube of a colorimeter and compared with a standard solution of sodium iodo-eosin. The results are expressed as mg. of iodo-eosin absorbed per sq. dm. of surface, and the values so obtained divided by 13·48 give the equivalent amount of Na_2O. As indicated by Mylius,[1] iodo-eosin reacts with other basic oxides as well as with the alkalis, particularly lead oxide, so that the results obtained do not strictly represent the alkali liberated, but they may be regarded as giving a comparative measure of the surface attack. For this reason, Elsden, Roberts and Jones[2] considered that a test on the broken surface after "weathering" for seven days in a saturated atmosphere at 18° was more reliable than a test on a freshly fractured surface.

The Report mentioned above gives the results of tests upon forty-seven optical glasses, comparing the iodo-eosin value obtained under three conditions, namely (*a*) a fresh fracture, (*b*) a "weathered" fracture, and (*c*) fractured under the iodo-eosin solution. All the glasses but three showed a diminution in iodo-eosin value after "weathering" as compared with the freshly fractured surface. The glasses were classified h^1 . . . h^5 as regards durability, according to the iodo-eosin values obtained for the "weathered" fractured surfaces, the limits of the various grades being as stated on p. 196.

The Dimming Test. Since the durability of an optical glass for practical purposes may be regarded as its power to keep its surface optically perfect and free from any decomposition products liable to give rise to tarnishing or dimming, the conditions requisite for a suitable test were worked out by Elsden, Roberts and Jones.[2] In order to get concordant results, special care must be taken in cleaning the specimen. The samples used were polished plates of glass $1\frac{1}{2}$ in. × $\frac{7}{8}$ in. × $\frac{1}{8}$ in. These were cleaned by being first washed with a mixture of redistilled alcohol and water to which 2 per cent. of acetic acid had been added, then rinsed in distilled water and dried with specially prepared linen cloths. After cleaning, the samples were carefully examined, both visually and microscopically, and again cleaned and dried. After momentarily heating in a flame to de-electrify them, they were placed immediately into the apparatus.

The linen cloths used were specially treated by boiling in a solution of pure sodium oleate in distilled water, then boiled repeatedly in distilled water until the water remained neutral to methyl orange, and finally in distilled water rendered just acid with acetic acid. The excess liquid was removed by wringing (the cloths being held in tongs) and the cloths were finally extracted in a Soxhlet apparatus with

[1] *Z. anorg. Chem.*, 1910, 67, 200. [2] *J. Soc. Glass Tech.*, 1919, 3, 56.

alcohol, after which they were allowed to dry slowly in a dust-free atmosphere.

The samples, cleaned as described, were inserted into a tube 11 in. × $1\frac{1}{8}$ in. together with one or more polished quartz plates, similarly cleaned, which served as controls. The tube was then placed in a thermostat regulated carefully to maintain a constant temperature of 80° and air, saturated at 80°, passed over the samples for thirty hours at a rate not exceeding 1 litre in three hours. At the conclusion of the period, the burner was removed from the water-bath and the water allowed to cool to 50° at the normal rate of cooling, after which the rate of cooling was accelerated by leading a stream of cold water to the bottom of the water-bath and siphoning off warm water from the surface at such a rate that the water level was maintained constant. The cooling was continued until the bath and its contents were about 2° below the room temperature, the rate of cooling being such that this took about three hours, the bath being continuously stirred and the current of air through the tube being maintained. The apparatus is designed to ensure that the air passing over the samples shall be saturated with moisture at the required temperature and shall be free from dust and acid or alkaline fumes.[1]

When the water-bath and the tube had cooled below the laboratory temperature, the tube and its contents were removed and the test pieces and quartz controls examined *in situ*. A slight formation of "dew" almost invariably appears on the test pieces, but if any such formation is apparent on the quartz controls the experiment is not satisfactory since this indicates either that these were not perfectly clean or that the cooling was not properly carried out, thus leading to a physical condensation of moisture on the surface from the saturated air, which is distinct from the chemical condensation due to the hygroscopic nature of the glass.

The glass specimens were removed from the cold tube and rapidly transferred to clean, dry test tubes, which were then closed with rubber stoppers. The visible "dew" disappeared rapidly in most cases; and the time taken for the disappearance gave a first indication of the quality of the glasses, poor glasses retaining the "dew" longer than the better ones.

The samples were then placed on clean, dry watch-glasses and the polished surfaces inspected carefully. With practice, especially when the polished specimens were viewed from various angles, very slight degrees of dimming could be observed. In extreme cases, with glasses of poor durability, the specimens may be no longer transparent.

After inspection by the naked eye, the specimens were examined microscopically, a 2/3 in. objective being recommended. The appearance

[1] For details of the actual apparatus used, see *J. Soc. Glass Tech.*, 1919, **3**, 57.

of the polished surfaces varied considerably. The surface may be covered with very fine particles, which may be uniformly distributed, or appear in patches, the intermediate areas being less affected. Larger particles with a crystalline outline may be in evidence, and drops of liquid may be seen, either irregularly distributed, or arranged more or less symmetrically in lines, the latter case probably indicating minute scratches formed during the polishing process. In the case of glasses of poor durability, actual pitting may be observed. After considerable experience, Elsden, Roberts and Jones[1] were able to classify the glasses examined according to the extent to which they were affected by the dimming test at 80° for thirty hours, as :—

1. Unaffected, or only slightly affected.
2. Decidedly affected.
3. Very seriously affected.

The distinction may be extended further by adding the sign, plus or minus, to indicate that the glass is rather more or less affected than the general standard of the class. Thus a glass classified as 2+ would be dimmed to a greater extent than the average standard of class 2 and yet considerably less than that of class 3. If only slightly less, the classification would be 3−.

It will be obvious that the personal factor enters rather largely into the classification, but with practice, different observers agree closely in the grading of the glasses.

Earlier attempts at discriminating between optical glasses were made by Zschimmer,[2] who compared the intensity of the spots produced on polished plates of the glass in twenty-four hours by a drop of a solution containing 0·5 per cent. acetic acid and 0·05 per cent. glycerine. A further test was to immerse one-half of a polished plate of glass in water for two to three days and then compare the appearance of the two halves.

The Autoclave Test. According to the Report of the British Scientific Instrument Association, 1921, the most suitable conditions for obtaining comparative results were to heat polished specimens in water for four hours at 4 atm. pressure (151°). The specimen pieces of glass were 3 cm. × 2 cm. × 0·5 cm. and polished on all faces. After thorough cleaning, the specimens were placed in silver trays covered with silica dishes and immersed in water. After autoclaving, the specimens were examined, first with the naked eye and second with a microscope. The losses in weight of the specimens were determined, and also the alkalinity of the solutions (by iodo-eosin). It was found that flint glasses were more stable than crown glasses, and that increase in the lead oxide content increased durability. The loss in weight did

[1] *J. Soc. Glass Tech.*, 1919, 3, 61. [2] *Deutsche Mechanikerzeitung*, 1903, 7, 53.

not always correspond to the alkalinity, as in many cases much of the products of decomposition remained on the surface of the glass.

The alkalinity of test surfaces, after autoclaving in steam, did not provide a satisfactory test owing to the extent of the corrosion experienced by certain crown glasses, even when the test was only carried out at 2 atms. (133°) for two hours.

6. **Crystal Glass.**—The term "crystal glass" is usually used to indicate the brilliant alkali-lead oxide-silica glasses which are used in the manufacture of "cut glass." As mentioned previously (see p. 192) the effect of lead oxide in a glass is beneficial from the point of view of durability, it being rather more effective in this direction than lime. Lead glasses are usually very durable, a glass containing 41·25 per cent. of PbO and 47·10 per cent. SiO_2 showing a greater resistance to the action of boiling water and to treatment in the autoclave at 183° than even laboratory ware, though rather less resistant to the action of alkaline solutions.[1] If it is desired to determine the durability of heavy lead glasses, a water test on a powdered sample (see p. 197) and an autoclave test as described on p. 201 would constitute the most suitable tests.

III.—THE ANALYSIS OF GLASS

The chief constituents of colourless and pale green glass are silica, and the oxides of calcium, sodium, potassium and lead. Alumina and magnesia in amounts varying from less than 0·25 per cent. to appreciable proportions occur in bottle glass and other glasses, and a small amount of arsenic oxide is present in many glasses. The oxides of barium, zinc, antimony, boron and phosphorus occur less frequently, and iron oxide (always present, owing to impurities in raw materials), selenium and the oxides of manganese, nickel and cobalt (as decolorisers), sulphur trioxide and chlorine (from impurities in raw materials or intentionally introduced as in plate glass) fluorine (from calcium fluoride; see p. 154) and titania occur as minor constituents.

In coloured or opal glasses, in addition to the constituents mentioned above, gold, silver, copper, carbon and sulphur, the oxides of tin, copper, chromium and uranium, and the sulphides of cadmium and other metals may occur. It should be noted that many of the substances mentioned above as minor constituents occur in opal and coloured glasses as major or essential constituents—for example, fluorine and sulphur trioxide (in certain opal glasses), and the oxides of iron, manganese, nickel and cobalt (in coloured glasses).

[1] Cauwood, Turner and Webb, *J. Soc. Glass Tech.*, 1918, **2**, 33.

In the schemes of analysis below, it is intended to deal chiefly with the constituents mentioned above, but it should be noted that many other substances may occur in glass. Sir Herbert Jackson[1] has stated "that with the exception of the rarer elements, all the chemical elements have been added to glass," and he has discussed the effects obtained by adding the oxides of zirconium, titanium and thorium.[2] H. J. Powell[3] has mentioned the introduction of didymium, erbium, iridium, thallium, vanadium, tellurium, lithium, and thorium into glasses, and has stated that a lithia glass proved very successful for the "windows" of X-ray tubes. Thallium oxide is present in certain special optical glasses.[4] Cerium oxide and titania have been introduced into heat-intercepting structural glass.[5] Special constituents also occur in eye-protective spectacle glasses which do not transmit ultra-violet rays and which give protection to the eye against glare; for such glasses, Sir William Crookes[6] used cerium, neodymium and praseodymium. Lepidolite, a mineral containing lithia-mica, has been advertised in the United States as a suitable general glassmaking material. If any of the constituents mentioned in this paragraph are suspected of being present in any glass to be analysed, an appropriate qualitative analysis should be made, and for the quantitative analysis, one of the methods below should be suitably modified to embrace the special constituents.[7]

Frequently it is not possible to know in advance what constituents are contained in the glass under examination. If the type of glass is known, some idea as to its probable composition can be obtained from the discussion on pp. 179-181. As the procedure to be adopted for the quantitative analysis of a glass depends upon the presence or absence of certain constituents, a preliminary qualitative analysis is often necessary, and it is particularly desirable to test qualitatively for acidic constituents other than silica.

SIMPLE PRELIMINARY TESTS

(*a*) *Dry Tests.* Not very much information can be gained by the application of dry tests to glass, but sometimes certain conclusions can be drawn from blow-pipe tests. If samples of glass in the form of splinters or rod are heated in a blow-pipe flame, under reducing conditions, and maintained in a soft state for one to two minutes, the appearance of the samples after cooling gives some indication of

[1] *J. Soc. Glass Tech.*, 1917, **1**, 140.
[2] *J. Soc. Arts*, 1920, **68**, 134.
[3] *J. Soc. Glass Tech.*, 1918, **2**, 241.
[4] *Sprechsaal*, 1915, **48**, 286.
[5] G. Alleman, *J. Soc. Chem. Ind.*, 1921, **40**, 241.
[6] *Phil. Trans.*, 1914, **214 A**, 1.
[7] For methods of determining such constituents, see J. W. Mellor, *A Treatise on Quantitative Inorganic Analysis*, 1913.

the composition of the glasses. With glass which contains lead, the surface of the sample is covered with a blackened iridescent film (due to metallic lead); from the intensity of the colouring of the film a rough approximation of the amount of lead present can be made, and this test will show the presence of as little as 0·25 per cent. of lead oxide. If, however, the lead glass examined is a hard glass, the film obtained is grey and less intensely coloured than with a soft glass of equal lead oxide content. Further, the presence in the glass of arsenic or antimony in appreciable amounts will cause the formation of a dark film in this test.[1] The test will not cause the formation of a dark film on a glass free from lead, arsenic and antimony, but owing to the effect of arsenic and antimony, the test cannot be relied upon for distinguishing between lead and lead-free glasses.

By the same blow-pipe test, green glasses coloured with chromium can be distinguished from those coloured with copper. A splinter of the glass is heated in a reducing blow-pipe flame to cause a bead to form on the end, and then heated for a further one to two minutes; the glass after cooling will show no change if coloured with chromium, but if coloured with copper the bead will show a brownish-red surface (due to the reduction of cupric oxide). The test is unreliable when the glass contains lead.

With red glasses, it is possible to distinguish between gold and copper colours by a blow-pipe test. A small piece of the red glass is heated in a glass tube, and the two drawn out together when soft. After cooling, the red colour is still evident in a gold ruby glass, but the sample is colourless if the glass is a copper ruby, as copper is more readily soluble. Another test, according to Lamplough[2] is to combine a piece of ordinary signal green glass with a ruby, when a gold ruby will show a purple colour, and a copper ruby a rather more green tint, due to a certain amount of green light which the latter allows to pass.

With experience, bottle glasses decolorised with selenium can be distinguished from those decolorised with manganese by viewing them in different lights: for, whereas the latter show very little difference in colour when brought from daylight to artificial light, preferably diffused, glasses decolorised with selenium appear distinctly lower in colour in artificial light; that is to say, a slightly pink glass will appear perfectly decolorised and a perfectly decolorised glass slightly green. When examining in artificial light the glass should not be viewed by transmitted light, but with the source of light at the back of the observer.

[1] Cauwood, Davidson, Hodkin and Turner, *J. Soc. Glass Tech.*, 1919, **3**, 266.
[2] *J. Soc. Glass Tech.*, 1922, **6**, 272.

(*b*) *Simple qualitative investigation* (*microchemical analysis*).[1] This investigation can be completed in one hour, and only requires a few milligrammes of glass; it is, therefore, useful when the sample has to be kept or when it is small.

Test 1. A drop of 10 per cent. hydrofluoric acid is placed on the glass. Immediate cloudiness shows the glass to be rich in *alkaline earths or heavy oxides* (CaO, BaO, PbO, ZnO). Some of the resulting mixture is cautiously introduced on the end of a clean platinum wire into a non-luminous flame; a fleeting green flash indicates the presence of *boric oxide*. The material on the platinum wire is heated to glowing; a yellow flame indicates *sodium* and a violet flame (seen through cobalt glass) *potassium*. A drop of hydrogen sulphide water is added to the remainder of the reaction products; a black coloration indicates *lead*.

Test 2. Another drop of 10 per cent. hydrofluoric acid is allowed to act on the glass for five minutes, then washed into a porcelain or, better, platinum crucible, with 3 c.c. water; a slight excess of sodium bicarbonate (about 0·1 g.) is added to the solution which is boiled for two minutes until a precipitate separates. After the precipitate has settled, the clear liquid is poured off and the precipitate washed by decantation three times with 3 to 5 c.c. water; then 10 drops of dilute hydrochloric acid is added to the residue and evaporated to dryness. The residue is treated with two drops of dilute hydrochloric acid and 3 c.c. water, warmed to dissolve the soluble portion and filtered. The insoluble residue is *silica*, and the filtrate contains the remaining constituents.

The filtrate is collected in a small test-tube. If Test 1 has shown lead to be present, it is removed by means of hydrogen sulphide. To the resulting filtrate is added one drop of dilute sulphuric acid and the mixture warmed; a heavy white precipitate indicates *barium*.

It is filtered off (if necessary) and then one drop of potassium ferrocyanide added; a slimy white precipitate indicates *zinc* (if bluish, some *iron* is present). If a precipitate is formed it is removed by filtration and the filtrate is heated to boiling with three drops of ammonia solution; a white gelatinous precipitate indicates *alumina* (and possibly *silica*). The mixture is now filtered (in any case) and a drop of oxalic acid solution is added to the filtrate and warmed gently; if *lime* is present, a white turbidity forms after about two minutes. After the complete separation of lime (if present), the presence of *magnesia* can be seen by the slow formation of a fine grained precipitate after the addition of two drops of sodium phosphate solution.

[1] Mylius and Groschuff, *Deutsche Mechanikerzeitung*, 1910, p. 41.

QUALITATIVE ANALYSIS

(a) Examination for all the Constituents except Silica, Boric Oxide, Fluorine and Chlorine

Method 1. About 5 g. of finely ground glass is decomposed with *pure* hydrofluoric acid and 5 c.c. of 50 per cent. sulphuric acid in the manner described on p. 225. The residue obtained on evaporation is then treated with hydrochloric acid and water, warmed and filtered if necessary. The insoluble residue (if any) and filtrate are examined separately.

Residue:—The possible constituents of the residue are silver chloride, barium and lead sulphates, metastannic and antimonic acids, selenium and gold. The residue may be coloured violet or red if gold or selenium is present.

To examine the residue:—(1) It is warmed with ammonia solution; silver chloride, if present, dissolves. The mixture is filtered and the filtrate tested for *silver*. (2) The remaining residue (if any) is boiled with strong ammonium acetate; lead sulphate, if present, dissolves. After filtration, if necessary, the filtrate is tested for *lead*. (3) The residue (if any) is boiled with strong sodium carbonate solution; barium sulphate, if present, is converted into barium carbonate and this, with any other residue, is filtered off (filtrate rejected), washed, and treated on the filter paper with warm dilute hydrochloric acid and the resulting chloride solution tested for *barium*. (4) If a white residue remains, it is treated as (5) below. If there is a violet or red coloured residue, it is heated first with concentrated nitric acid to remove selenium and then with aqua regia to remove gold. The solution obtained by the latter treatment is tested for *gold*. As regards selenium, the procedure described below may be used to test the solution obtained by the concentrated nitric acid treatment, but it is advisable to test for selenium in a separate sample of glass, as described below. (5) If any residue still remains it is fused with sodium carbonate and sulphur. The melt is extracted with water, filtered and the filtrate tested for *tin* and *antimony*.

Filtrate:—This is tested by the ordinary methods[1] used for the qualitative analysis of inorganic substances, tests being made for phosphoric oxide and basic constituents.

Method 2. If the glass is known or suspected to contain lead or

[1] For methods of qualitative analysis reference to the following can be recommended:—Noyes and Bray, *J. Amer. Chem. Soc.*, 1907, **29**, 137, or *Chem. News*, 1907, **95**, 89, etc.; Noyes, Bray and Spear, *J. Amer. Chem. Soc.*, 1908, **30**, 481, or *Chem. News*, 1908, **98**, 6, etc.; Bray, *J. Amer. Chem. Soc.*, 1909, **31**, 611. These papers discuss the making of separations, the completeness of such separations and the possible limits of detection. The elements dealt with include the more and also the less common ones such as beryllium, uranium, vanadium, titanium, zirconium and thorium.

barium, the sample for the qualitative analysis can advantageously be decomposed with hydrofluoric and nitric acids as described on p. 226. The residue after the final evaporation with nitric acid is dissolved in dilute nitric acid, filtered if necessary, and the resulting residue (if any) and filtrate are examined separately. It should be noted that in this method the possible constituents of the insoluble residue are metastannic and antimonic acids and gold, while silver, lead, barium and selenium pass into solution. The residue (if any) is tested for gold, tin and antimony by the procedures discussed in method 1, and the filtrate is qualitatively analysed by the usual methods (see footnote, p. 219).

Sulphur trioxide can be tested for in a portion of the above filtrate. It will be present if the glass contains dissolved sulphates, and it may be found if the glass under examination is one coloured by sulphides or sulphur. The purity of the reagents used in this and following tests should be checked. When testing for minor constituents, either qualitatively or quantitatively, the importance of using pure reagents and of an accurate knowledge of the blank cannot be exaggerated.

Sulphur, Sulphides and Carbon. No really satisfactory methods are as yet available for the detection of sulphur (as such), sulphides (as such) and carbon in glass, although many commercial glasses are coloured with these materials and further reference to them is made on p. 276 in the section on the quantitative analysis of coloured glasses.

Selenium can be tested for in the following manner:—To 2 to 3 g. of finely ground glass, placed in a platinum crucible, 15 to 20 c.c. of hydrofluoric acid and 2 c.c. of strong nitric acid are added. The solution is evaporated to dryness on a water-bath at a temperature of about 90°, with occasional stirring with a platinum wire during the early part of the evaporation. To the residue, after evaporation, 4 to 5 c.c. of strong nitric acid is added and the solution again evaporated to dryness. The procedure then depends upon the type of glass under examination, as follows:—

(1) With ruby glasses, the residue is transferred with a minimum amount of water to a small porcelain basin, the water evaporated off, the residue dissolved in strong hydrochloric acid, and stannous chloride added, or sulphur dioxide gas passed in to saturation. A brick-red coloration or precipitate is formed if selenium is present.

(2) With decolorised bottle glasses,[1] the residue is dissolved with 5 c.c. of nitric acid and transferred to a 100 c.c. beaker with as little water as possible. The resulting solution is then divided into two equal portions and each part treated separately as follows:—

(*a*) Small quantities of selenium can be detected in strong sulphuric acid solution by means of codeine, but manganese interferes with the

[1] See "The Detection of Selenium in Decolorised Bottle Glasses," Bowmaker and Cauwood, *J. Soc. Glass Tech.*, 1927, 11, 386.

test. Therefore, the first half of the solution (placed in a 100 c.c. beaker) is made up to 50 c.c. in volume by the addition of 1 : 1 nitric acid and then tested for manganese by adding 10 c.c. of $N/100$ silver nitrate solution, and 0·5 g. ammonium persulphate, the beaker then being stood on a hot plate. When the solution becomes hot, the pink colour of permanganic acid will appear if manganese is present.

(*b*) When manganese is absent, the second portion of the glass solution is treated with 10 c.c. sulphuric acid, evaporated until fumes of sulphuric acid have been evolved for about two minutes, and then cooled. When *quite cold*, a piece of codeine sulphate about the size of a pin's head is added and stirred until dissolved, the solution then being heated to the fuming point, when a green coloration denotes the presence of selenium.

When, on the other hand, manganese is present, the solution from the glass is diluted to about 60 c.c. and bromine water added until the colour is fairly strong. The solution is then made faintly alkaline with ammonia brought rapidly to the boil and filtered. The precipitate, which contains the manganese, is washed once with hot water and then rejected. To the filtrate and washings, after cooling, 10 c.c. of sulphuric acid are added, the solution evaporated on a hot plate until the sulphuric acid has fumed for a few minutes and then stood aside to cool. *When quite cold* the codeine test is applied, as described in the above paragraph.

To detect small amounts of selenium successfully with codeine, it is important to use only the small quantity of codeine sulphate specified above and to add it to the sulphuric acid solution when *quite cold*.

(b) Examination for Silica, Boric Oxide, Fluorine, Chlorine.

About 2 g. of finely powdered glass is fused with about 8 g. of sodium carbonate. The resulting melt is digested (preferably in a platinum basin) with about 50 c.c. of hot water and when all the soluble portion has dissolved, the residue is filtered off and washed, the total filtrate and washings being kept to a volume of about 100 c.c. The filtrate contains the silica, boric oxide, fluorine and chlorine (also any phosphoric oxide and sulphur trioxide) present in the glass and can be used for testing for these constituents as follows:—

Silica. An examination for this is rarely made, but when necessary it can be carried out on a small portion of the filtrate in the usual way, as also for *chlorine*.

Fluorine. To another fairly large portion of the filtrate, solid ammonium carbonate is added and the mixture is digested in a warm place. After standing some time, the precipitate is filtered off and the

filtrate evaporated to a small volume. Sufficient acetic acid solution is then added to give an excess of a few c.c. of 3 N acid after neutralising the alkaline carbonate present, and the solution is warmed to expel carbon dioxide. Calcium chloride is added, the solution allowed to cool and put aside for some time. When fluorine is present, a white precipitate of calcium fluoride forms. If a precipitate is deposited after a time, it is collected upon a small filter paper, dried and then separated from the filter (by incineration if necessary) for confirmation of fluorine, *e.g.* by an etching test,[1] or it may be used as follows: The precipitate is mixed with two or three times its volume of finely ground quartz and transferred to a dry test-tube. Sufficient concentrated sulphuric acid to make a thin paste is added from a tube, care being taken not to wet the sides of the test tube. A piece of narrow glass tube, wet on the inside but dry on the outside, is inserted in the test tube and supported with a rubber stopper or other arrangement so that it extends to within about one inch from the bottom. The mixture is warmed over a small flame (not enough to vaporise the sulphuric acid) for a minute or two. The formation of a white precipitate in the wet part of the inner tube confirms the presence of fluorine.

Boric Oxide. Another portion of the filtrate is concentrated by evaporation to about half its original volume, cooled and neutralised with 1 : 1 sulphuric acid. A few c.c. of strong sulphuric acid are added and some ethyl alcohol. The mixture is stirred, the alcohol ignited and, if boric oxide is present, it burns with a greenish flame. Alternatively, a turmeric test[2] may be applied for boric oxide. Bertrand and Agulhon[3] have used turmeric paper tests for boric oxide with success and, by comparison with standards, such tests can be made to yield fairly accurate quantitative results.

If thought desirable, a separate sample of glass can be used for testing for each of the above constituents. It is the usual practice to use a separate sample for boric oxide, and then the following tests are readily applied:—(1) A quick test may be made by mixing some ground glass into a paste with hydrofluoric acid and sulphuric acid, or with calcium fluoride and sulphuric acid, and using the paste for a flame test. If, however, copper or barium is present, the following alternative procedure is used. (2) About 1 g. of the finely powdered glass is added to hydrofluoric acid in a platinum crucible, stirred with a platinum wire and then evaporated to dryness on a water-bath. After cooling, a few drops of concentrated sulphuric acid are added

[1] Woodman and Talbot, *J. Amer. Chem. Soc.*, 1906, **28**, 1437.

[2] See Noyes, *Qualitative Chemical Analysis of Inorganic Substances*, New York, 1922, for a test which will detect ½ mg. of boric oxide.

[3] *Comptes rend.*, 1913, **157**, 1433.

and the whole well stirred. The crucible is then covered with the lid so as to leave a narrow opening, placed upon a triangle and carefully heated by means of a Bunsen burner provided with a rose-piece, while at the same time a non-luminous flame is so held over the crucible that the vapours escaping through the opening must pass this flame. If boric oxide is present, a more or less vivid green coloration of the flame takes place after heating for a short time. By this test 0·1 per cent. of boric oxide can be detected and with practice the test can be made during the decomposition of the glass for the qualitative analysis of the bases. Copper and barium, if present, do not interfere with this test.

Quantitative Analysis

Preparation of the Substance for Analysis. Usually glasses to be examined are homogeneous and, therefore, sampling presents no difficulties. When an average composition of mixed cullet is required, ordinary sampling procedures are followed. If the sample or article to be examined is built up of two or more kinds of glass, as is the case with certain coloured decorative ware, etc., methods of sampling depend on the nature of the investigation and on the particular article.

In order to reduce the glass to a fine state of division preparatory for analysis, the simplest plan is to heat it strongly and then to chill suddenly with water, crush it in a smooth porcelain mortar until it will all pass through a fine gauze, and finally grind it in an agate mortar until no coarse particles remain. When traces of metallic oxides are to be determined, a metal sieve should not be used. Glass need not be powdered especially finely for complete decomposition on fusion with alkali carbonates, or on treatment with hydrofluoric acid, but a difficultly fusible glass should be powdered to a fine state for an alkali carbonate fusion. For the determination of alkali oxides by the Lawrence Smith method (see p. 235) a very finely ground sample is necessary. In exact analyses, very fine grinding is disadvantageous, because owing to the abrasive nature of glass it becomes contaminated with material from the pestle and mortar. Hempel[1] tested the effect of grinding glass very finely in mortars of agate, hardened steel and glass, and found that least contamination occurred with hardened steel and most with agate. A hardened steel mortar, however, can only be used in preparing glass samples for analysis when the determination of the iron oxide in the glass is not required. Ferguson and Hostetter[2] recommend the use of a brass cylinder in conjunction with an agate

[1] *Z. angew. Chem.*, 1901, **14**, 843.
[2] *J. Amer. Ceram. Soc.*, 1919, **2**, 608.

pestle for the preliminary crushing of samples for iron oxide determinations.

When an exact determination of iron is unimportant, the sample can quickly be reduced to a fine state as follows:—Crush the sample to small pieces on a hard steel plate (preferably surface hardened) with a hard steel hammer or weight; transfer the pieces to a hard steel diamond mortar and reduce the size of the particles until they will pass through a fine gauze, finally grinding in an agate mortar. The powdered glass obtained by this method is slightly contaminated with iron, but if the preparation of the sample is carried out according to the details given by Hillebrand [1] the contamination is very small.

Analyses are usually carried out on samples which have been dried to constant weight at about 105°. With certain hygroscopic glasses, a determination of absorbed moisture can be carried out if desired by heating a sample at 600° to 700°. All technical glasses contain traces of absorbed moisture and gases, which are usually ignored in a chemical analysis, and this may partly account for the fact that in complete analyses of glasses low in alumina the total of the percentages found is, on the average, less than 100 per cent.[2]

Decomposition for Analysis. Two or more decompositions are necessary for a complete glass analysis, and various reagents have been suggested for this purpose. These include sodium carbonate, a mixture of sodium and potassium carbonates (fusion mixture), sodium bicarbonate,[3] boric oxide, lead oxide, lead carbonate, bismuth oxide, hydrochloric acid under pressure at temperatures up to 400°,[4] hydrofluoric acid in conjunction with a mineral acid,[5] calcium carbonate with ammonium chloride, and sodium peroxide. Of the above, the fluxes recommended by Jannasch and his pupils,[6] namely, boric oxide, lead oxide, lead carbonate and bismuth oxide are very rarely used in glass analysis, although with certain glasses they offer a rapid and convenient method for some determinations.

The reagents generally used for decomposition in glass analysis are:—

(1) Sodium Carbonate. This is now preferred to fusion mixture, because potassium salts are more difficult to wash out of precipitates than sodium salts. In some cases, for example in arsenic determinations, it is advisable to use a small amount of nitrate mixed with the sodium carbonate.[7] The sodium carbonate used must be pure, and in

[1] *Bulletin* 700, *U.S. Geol. Survey*, 1919, pp. 57-64.
[2] See Allen and Zies, *J. Amer. Ceram. Soc.*, 1918, **1**, 739.
[3] Holthof, *Z. anal. Chem.*, 1884, **23**, 498; *Chem. News*, 1885, **51**, 18.
[4] Jannasch, *Ber.*, 1891, **24**, 273; *Z. anorg. Chem.*, 1894, **6**, 72.
[5] Berzelius, *Pogg. Ann.*, 1838, **44**, 134; Hinden, *Z. anal. Chem.*, 1906, **25**, 332, etc.
[6] Jannasch, *Praktischer Leitfaden der Gewichts-analyse*, Leipzig, 1904.
[7] Allen and Zies, *loc. cit.*

exact work the purity should be checked by the tests given in Vol. I., p. 561. Samples of glass are decomposed by fusion with sodium carbonate for the determination of silica, boric oxide, fluorine and other acidic constituents, and in many cases for the determination of the basic oxides other than the alkali oxides.

(2) Hydrofluoric Acid. This can be used in conjunction with sulphuric, nitric, oxalic, or perchloric acid. Oxalic acid is used in a rapid method, described on p. 258, due to Sullivan and Taylor.[1] Perchloric acid has been recommended by Lundell and Knowles.[2] Decomposition by hydrofluoric acid and another acid possesses many attractive features; it is comparatively rapid and easy to carry out, and as about 70 per cent. of the glass is usually driven off as silicon tetrafluoride or boron trifluoride, it is possible to decompose fairly large samples and so obtain a solution in which minor constituents can be determined with accuracy. Further, owing to the removal during decomposition of any silica, boric oxide and fluorine present in the glass, the method is advantageous for the rapid estimation of basic oxides without interference from boric oxide and fluorine. Disadvantages of this method of decomposition are (1) the possibility of deleterious impurities in the hydrofluoric acid[3] interfering with subsequent operations (only the purest acid obtainable should be used, and its purity should be checked by suitable tests); and (2) the difficulty of completely expelling the hydrofluoric acid; incomplete removal leads to an error in the alumina determination. For these reasons, the sodium carbonate decomposition is preferred for accurate analyses.

Owing to its higher boiling-point, sulphuric acid is used instead of nitric acid in conjunction with hydrofluoric acid whenever possible, and the decomposition is carried out according to one of the following methods:—(*a*) A sample of glass (usually 1 to 2 g.) is weighed out in a platinum crucible of 30 to 40 c.c. capacity and moistened with a little water. Pure hydrofluoric acid (15 to 20 c.c.) is added, the mixture stirred with a platinum wire and allowed to stand (covered) on a water-bath until decomposition of the glass is complete. A sufficient, but not too large, excess (say about 4 c.c.) of sulphuric acid (1 : 1) is then cautiously added and the whole is gently evaporated almost to dryness, precautions being taken against loss by spurting. For such evaporations, the use of a radiator, such as that recommended by Hillebrand,[4] is very convenient. If the glass sample is a large one (as in the determinations of certain minor constituents), or if it is important to ensure the complete expulsion of silica, the evaporation is stopped

[1] *Ind. Eng. Chem.*, 1914, **6**, 897, and *Chem. News*, 1915, **111**, 64.
[2] *J. Amer. Ceram. Soc.*, 1927, **10**, 829. [3] Allen, *Analyst*, 1896, **21**, 87.
[4] *Bulletin* 700, *U.S. Geol. Survey*, 1919, p. 33.

when fumes of sulphuric acid appear, the crucible and contents cooled, more hydrofluoric acid (say 5 to 10 c.c.) added, evaporation recommenced and this time carried almost to dryness. It is essential that the final evaporation should be prolonged almost to dryness in order to expel completely the hydrofluoric acid and volatile fluorides; to ensure this expulsion, Hillebrand[1] recommends repeated evaporations with small portions of sulphuric acid as a final treatment in this decomposition. Except in special cases, the final residue when cool is treated with about 5 c.c. strong hydrochloric acid and about 10 c.c. hot water, and after warming gently for some time, transferred to a beaker in which the mixture is diluted and the soluble portion completely dissolved by gentle boiling.

(*b*) For rapid analyses, 1 to 2 g. of the ground glass is moistened in a platinum crucible with a little water, 15 to 20 c.c. pure hydrofluoric acid and about 4 c.c. sulphuric acid (1 : 1) are added and the whole is at once slowly evaporated until fumes of sulphuric acid appear. After the sulphuric acid has fumed for a few minutes, the crucible and its contents are allowed to cool, then a further 10 c.c. of hydrofluoric acid is added and an evaporation almost to dryness is cautiously carried out. (*Note.*—Some analysts consider one evaporation with hydrofluoric acid to be sufficient, but in order to ensure complete expulsion of silica two evaporations are very advisable.) With a large sample, greater quantities of hydrofluoric acid are usually employed. The final residue is generally dissolved in hydrochloric acid and hot water, as described above.

One disadvantage attending the use of sulphuric acid for decomposing a sample is that, according to Mellor,[2] the sulphates formed interfere with the complete precipitation of alumina by ammonia. By continuing the evaporation almost to dryness, this interference is reduced to a minimum.

When the glass to be examined contains lead or barium, it is sometimes advantageous to use nitric acid instead of sulphuric acid. A sample of powdered glass can be decomposed with hydrofluoric and nitric acids as follows:—The sample (usually 1 to 2 g.) is weighed into a platinum crucible of about 30 c.c. capacity, moistened with a little water, about 15 c.c. hydrofluoric acid and 5 c.c. nitric acid (1 : 1) added, the mixture stirred with a platinum wire, and the crucible then allowed to stand (covered) on the water-bath to promote decomposition of the glass. After standing about twenty minutes, the cover is removed, and the contents of the crucible are slowly evaporated almost to dryness. After cooling, a further 10 c.c. of hydrofluoric acid and 5 c.c. nitric acid (1 : 1) are added, and evaporated on the water-bath to dryness. The

[1] *Loc. cit.*, p. 137.

[2] *A Treatise on Quantitative Inorganic Analysis*, 1913, p. 180.

residue so obtained is subjected to three further evaporations to dryness with 3 to 4 c.c. of concentrated nitric acid, because it is difficult to expel hydrofluoric acid completely with nitric acid unless repeated evaporations are made. (If a large sample of glass is to be decomposed, a platinum dish and larger quantities of acid are used.) The final residue is usually taken up with nitric acid and hot water.

(3) Calcium Carbonate with Ammonium Chloride. Glass is decomposed with these reagents for the estimation of alkali oxides by the Lawrence Smith method (see p. 235).

(4) Sodium Peroxide. This is sometimes a convenient reagent for the decomposition of (1) glasses containing large amounts of arsenic, antimony or tin; and (2) certain glass enamels.[1]

A. Colourless or Pale Green Glasses

1. Silicate Glasses free from Lead and Barium

The methods in this section apply to glasses whose main constituents are silica, alumina, lime, magnesia, and the oxides of sodium and potassium. The minor constituents dealt with are the oxides of arsenic, antimony, iron, titanium, manganese, nickel and cobalt; selenium, sulphur trioxide and chlorine. Such glasses as window glass, so-called Bohemian glass, and practically all colourless or pale glass used for the manufacture of bottles and containers can be analysed by the methods described below. Other minor constituents occasionally found in bottle glass include fluorine and boric oxide. Fluorine, if present, can be determined by the method described on p. 262. If the amount of it is small, say less than 0·3 per cent., the other constituents of the glass can be determined by the methods given in this section, but if large, the methods described on p. 262 must be used. Boric oxide, if present, is determined as described on p. 249, the other constituents being determined by the methods given below after removing the boric oxide during the silica evaporation as described on p. 245.

Other major constituents which might occur in the types of glasses mentioned above are barium oxide and zinc oxide. Barium oxide is sometimes introduced into bottle glass made in pots, and it is an occasional constituent of glass for pressed ware; if barium oxide is present in any glass under examination, the analytical procedure has to be modified as described on p. 256. Zinc oxide is a very unlikely constituent of the commercial glasses mentioned above, but special "silicate glasses free from lead and barium" containing zinc oxide have been prepared; if zinc oxide is present, the methods described on p. 245 must be employed for the analysis.

[1] See Mellor, *A Treatise on Quantitative Inorganic Analysis*, 1913, pp. 244, 266 and 475.

Major Constituents

Silica.—One g. of the powdered glass sample is weighed out in a platinum crucible of about 30 c.c. capacity, and 5 g. of pure dry sodium carbonate added in three or four portions, mixing with a small spatula or smooth glass rod after each addition, any adhering particles being finally brushed into the crucible. A thin layer of sodium carbonate is then spread on top of the mixture. The crucible, covered with the lid, is then placed in a slightly inclined position on a platinum or pipeclay triangle and heated for fifteen minutes over a low flame, so that the bottom of the crucible is at a dull red heat for about a quarter of its length. If the crucible and its contents are heated too strongly at the beginning, the reaction is too violent and the effervescence resulting from the rapid escape of carbon dioxide from the semi-molten mixture may cause the mass to overflow from the crucible. After the preliminary gentle heating for about fifteen minutes, the temperature is gradually raised and finally the crucible and its contents are subjected to the full heat of a Méker or Teclu burner until the mass is in a state of quiescent fusion and no more gas bubbles are evolved. The flame of the burner should never be allowed to envelop the crucible completely, as the atmosphere inside the crucible should be kept as oxidising as possible. When fusion is complete, the crucible is removed by platinum-tipped tongs, the bottom dipped into cold water in a dish (no water must splash into the crucible) and, as the contents begin to solidify, a rotary motion is given to spread the melt over the sides and bottom of the crucible. When quite cold, the crucible is about half filled with hot water and heated gently without allowing the contents to boil. Usually the cake quickly becomes loose and it is then transferred to a 250 c.c. porcelain basin. Alternatively, a stout piece of platinum wire of convenient length and bent at the end into a loop is introduced into the fused mass, which is then allowed to cool. When the mass has so far cooled as to grip the loop of platinum wire the crucible is again rapidly heated to melt only a thin layer next the crucible, and the cake is withdrawn by gentle pulling and transferred to the basin.

A melt coloured appreciably blue-green indicates the presence of manganese. (For very accurate work, a platinum basin should be used and any sodium manganate present should be decomposed by the addition of a few drops of alcohol before hydrochloric acid is added.) The cake is treated with about 100 c.c. of hot water, the basin covered with a clock-glass and heated on the water-bath for about ten minutes to soften the cake and dissolve as much as possible, and then about 20 c.c. of concentrated hydrochloric acid is added slowly from a pipette, heating (covered) on the water-bath being continued. From time to

time the disintegration of any undecomposed portions of the cake is assisted by means of a glass rod with fused end, and when effervescence finally ceases, the clock-glass is washed down and removed. The crucible and lid are cleaned with hot dilute hydrochloric acid and a "policeman" and the washings added to the contents of the basin, which are then evaporated to dryness.

When the mixture becomes pasty during the evaporation, it is repeatedly stirred with a short glass rod, and all crusts and lumps are gently broken up. The heating on the water-bath is continued until the residue smells only very faintly of acid. After cooling, the mass is moistened with concentrated hydrochloric acid, about 50 c.c. of hot water added, and the basin and contents again heated on the water-bath. After stirring to dissolve the soluble chlorides, the silica is digested for about ten minutes, and then filtered, first by decantation, leaving nearly all the silica in the bottom of the basin. The silica is generally in a coarse condition and may be crushed finer with a pestle or a "policeman," to assist washing; it is twice digested with about 25 c.c. hot water slightly acidified with hydrochloric acid, after which it is transferred to the filter and washed with hot water until the washings are free from chlorides. For very accurate work, it is advisable to wash with cold water.

The filtrate, which contains 1 per cent. or more of the silica present, is returned to the basin used for the first evaporation and again evaporated to dryness on the water-bath. When the smell of acid has practically disappeared, the residue is heated in an air oven for about thirty minutes at 105° to 110°. After cooling, the residue is moistened with concentrated hydrochloric acid, 40 to 50 c.c. hot water added, the soluble chlorides dissolved, the mixture heated on the water-bath for about ten minutes and then filtered through a small filter paper. The small precipitate of silica is washed free from chlorides with cold water. It is advisable to note the amount of hydrochloric acid used in dissolving the residue after this second evaporation treatment, owing to the importance of the ammonium chloride concentration during the subsequent alumina precipitation.

The two moist filter papers and precipitates are transferred to a weighed platinum crucible (the larger precipitate being placed underneath), carefully dried and charred *without flame* over a small Bunsen flame placed some distance below the crucible. The carbon is burnt off slowly and then the crucible and contents, with the lid on, are heated over a strong blast or its equivalent for twenty to thirty minutes and afterwards cooled in a desiccator and weighed. Unless strongly ignited, the silica precipitate is very hygroscopic; in any case it is advisable to re-ignite, cool and re-weigh. The weighed precipitate is moistened with 3 to 5 c.c. of water, a few drops of

concentrated sulphuric acid and 10 to 15 c.c. pure hydrofluoric acid added and the whole cautiously evaporated to dryness. The crucible and residue are strongly ignited, cooled and weighed. The residue consists of impurities in the silica precipitate and its weight is deducted from the weight of the impure silica to obtain the true weight of silica.

The residue from the silica usually consists chiefly of alumina, titania and iron oxide. With glasses containing large amounts of alumina, or when the alumina determination is unimportant, it is customary to ignite the precipitates of alumina, etc. (see below), in the crucible containing the residue from the silica, and to count that residue as part of the alumina, iron oxide and titania. In exact work or when the alumina determination is important, the residue is fused with a small amount of sodium carbonate, the melt dissolved in hydrochloric acid and the solution added to the filtrate from the silica.

For technical purposes, two evaporations for silica are sufficient, but a small amount of silica still remains in solution after the second evaporation. Nearly the whole of this silica can be removed from the alumina later, but for *very* accurate work, a third evaporation is advisable, which must be carried out in platinum.

Alumina, Iron Oxide and Titania.—These constituents, together with the lime and magnesia, are present and can be determined in the filtrate from the silica. If the glass under examination contains neither arsenic nor antimony, one can proceed direct to the precipitation of the alumina, iron oxide and titania. Otherwise the arsenic and antimony are precipitated with hydrogen sulphide, the precipitate filtered off, washed and then rejected, because arsenic and antimony trichlorides (if present) volatilise partly, and occasionally almost completely, during the evaporations to dryness for the determination of silica. (For the determination of arsenic and antimony, see p. 236.) The combined filtrate and washings are boiled till free from hydrogen sulphide, and then boiled with a few drops of nitric acid to oxidise any iron present.

The solution from which the alumina is to be precipitated should be adjusted to a bulk of 200 to 250 c.c. Ammonium chloride is added in sufficient quantity to hold in ammoniacal solution the magnesium and any manganese present, and to obtain the proper conditions for the quantitative precipitation of alumina, usually 2·5 g. per 100 c.c. being used. Blum[1] recommends the use of at least 2 to 5 g. ammonium chloride per 100 c.c. of solution. A few drops of 0·2 per cent. alcoholic methyl red solution are then added, the solution is heated just to boiling and ammonia (free from carbonate) added drop by drop with constant stirring until the colour of the indicator changes to a distinct

[1] *J. Amer. Chem. Soc.*, 1916, 38, 1282.

yellow. The mixture is boiled for one to two minutes and then filtered immediately. The precipitate is washed four or five times with hot 2 per cent. ammonium nitrate solution. If small, the precipitate is then dissolved by pouring hot dilute hydrochloric acid (1 in 4) through the filter and the solution is collected in the beaker used for the first precipitation. If large, the filter is punctured at the bottom by means of a glass rod and the precipitate washed through with a fine jet of hot water and collected in the beaker used for the first precipitation, where it is dissolved in hot dilute hydrochloric acid (1 : 1). The last traces of precipitate are removed from the filter by washing with hot dilute hydrochloric acid (1 : 3), the washings being collected in the beaker containing the main portion of the precipitate. In either case, the filter paper is washed free from chlorides and saved for ignition later. The alumina, etc., is reprecipitated with ammonia in the presence of ammonium chloride as above, filtered, and washed with small quantities of hot 2 per cent. ammonium nitrate solution until free from chlorides.

The filtrate from the second alumina precipitate is combined with the first filtrate, the whole made slightly acid, and evaporated to 150 to 200 c.c. in a porcelain (or platinum) basin. Ammonia is then added to make the solution slightly alkaline and, after heating a further short time, the mixture is filtered immediately through a small paper to remove the precipitate of alumina (and silica) which forms. To reduce the quantity of ammonium salts in solution, the filtrate from the second alumina precipitate may be evaporated to dryness, gently ignited to remove ammonium salts and the remaining residue taken up with dilute hydrochloric acid and added, whether wholly soluble or not, to the first filtrate, after which the recovery of the last trace of alumina proceeds as above. The filtrate from the alumina scum is collected and reserved for the determination of lime, etc.

The moist filter papers and precipitates are transferred to a weighed platinum crucible, dried and ultimately ignited strongly for fifteen minutes, the various operations being similar to those used with the silica filters and precipitates. The precipitate should be weighed, covered, and then re-ignited and re-weighed rapidly (covered), owing to its very hygroscopic nature. The precipitate contains alumina, iron oxide, small amounts of silica and titania and possibly traces of manganese. In approximate analyses, it is usually sufficient to record the combined percentage of this precipitate plus the residue from the silica (see above) as "alumina, etc." In exact analyses, the iron oxide, silica and titania in the precipitate are determined (manganese, if present, is usually negligible) and the alumina is obtained by difference.

The precipitate of alumina, etc., is examined (when necessary) by fusion with eight times its weight of potassium bisulphate or pyrosulphate

(for details see p. 240), and the iron oxide and titania determined colorimetrically in the final filtrate, as described on pp. 241 and 171. In exact analyses, the result for iron oxide should be used only for the purpose of determining alumina by difference, and an exact iron determination should be made on a separate sample as described below. Titania is very rarely determined in the glasses dealt with in this section, but if an accurate result for alumina by difference is required, titania must be determined, as it is usually present.

The fusion of the alumina precipitate with potassium bisulphate or pyrosulphate may be omitted when the precipitate is small if it is permissible to report the combined percentage of alumina, iron oxide and titania. The contained silica is then determined by evaporating the precipitate to dryness with hydrofluoric and sulphuric acids, followed by strong ignition and re-weighing. In twenty-five analyses of bottle glass containing about 0·45 per cent. alumina and iron oxide, the average amount of silica found in the alumina precipitate by this means was 1 mg. for 1 g. of sample (Cauwood).

Oxides of Manganese, Nickel and Cobalt.—The colourless (decolorised) glasses dealt with in this section may contain one or more of the following decolorising agents (nickel being the most rarely present), the usual percentages being of the following order:—

Cobalt oxide	0·0001 per cent.
Nickel oxide	0·005 to 0·01 per cent.
Selenium	0·001 per cent.
Manganese oxide	0·25 per cent.

In the main analysis, the presence of selenium, nickel and cobalt can be ignored, but manganese (if present) has to be separated if accurate lime and magnesia determinations are required.

The manganese is precipitated in the filtrate from the alumina: (*a*) by ammonia and bromine; or (*b*) by ammonium sulphide. Precipitation with ammonia and bromine is the method usually employed, but according to Hillebrand[1] satisfactory precipitation with ammonium sulphide may be carried out as follows:—The solution (reduced to about 130 to 150 c.c. in bulk) is placed in a 200 c.c. flask, 2 or 3 c.c. strong ammonia added and hydrogen sulphide is passed in to saturation. A second like amount of ammonia is then added, the flask filled to the neck by the addition of water, cooled and set aside for at least twelve, and preferably twenty-four hours or longer. The precipitate is then collected on a small filter and washed with water containing ammonium chloride and sulphide, the filtrate being retained for the determination of lime and magnesia.

In exact analyses, manganese (if present) is determined in a separate sample (as below) and the manganese precipitate obtained

[1] *Bulletin* 700, *U.S. Geol. Survey*, 1919, p. 135.

by either of the above methods is rejected, after washing, because the precipitation is not quantitative and the precipitate may be impure, errors which usually do not balance. For less exact analyses (*a*) the manganese precipitate obtained by means of ammonia and an oxidising agent is washed with hot 2 per cent. ammonium nitrate solution, ignited and weighed as Mn_3O_4, or (*b*) the manganese sulphide precipitate is dissolved in hydrochloric acid and the hydrogen sulphide boiled off; the manganese is reprecipitated with sodium carbonate, filtered off, washed, ignited, weighed as Mn_3O_4 and reported as such.

For some purposes it is satisfactory to precipitate the alumina and oxides of iron and manganese together with ammonia and bromine, and report the combined percentage of that precipitate plus the residue from the silica as "Alumina, Iron Oxide and Manganese Oxide."

Lime.—If manganese is absent, the filtrate from the alumina precipitate is diluted, if necessary, to 250 to 300 c.c. (to ensure a sufficient dilution of any magnesia present), boiled for a few minutes with 2 to 3 g. of ammonium oxalate and 2-3 c.c. of strong ammonia, heated on a water-bath for one to two hours and then put aside to cool. Calcium oxalate is precipitated and after standing at least four hours the clear liquid is poured through a filter paper, the precipitate washed three or four times by decantation with dilute ammonia (1 : 10) or 1 per cent. ammonium oxalate solution and finally transferred to the filter with cold water. If the glass contains manganese, the calcium is precipitated in a similar manner in the filtrate from the manganese, without previous removal of any ammonium sulphide present. The calcium precipitate then frequently contains traces of manganese, which can be determined colorimetrically (see p. 238) after weighing the lime if *great* accuracy is required. In either case, if much magnesia is present more ammonium chloride should be added before precipitating the calcium.

In exact analyses it is necessary to reprecipitate the calcium to obviate contamination with alkali chlorides and, possibly, magnesia. The calcium oxalate precipitate is dissolved through the filter with hot dilute nitric acid (1 : 5) and the filter thoroughly washed and saved for ignition, the solution being collected in the beaker used for the first precipitation. The calcium is reprecipitated as above, but from an ammoniacal solution *small in bulk*, and with the addition of only a few crystals of ammonium oxalate. After standing for at least four hours, the second calcium oxalate precipitate is filtered off, washed free from chlorides with cold 1 per cent. ammonium oxalate solution, and eventually ignited to calcium oxide (lime) for weighing, care being taken to prevent burner gases passing into the crucible during the ignition. In less exact analyses, the first precipitate is completely transferred to the filter, washed with cold water, and either ignited

to lime and weighed, or dissolved in warm dilute sulphuric acid (1 : 5) and titrated warm with standard potassium permanganate solution.[1]

Magnesia.—To precipitate magnesium, the filtrate from the calcium oxalate is boiled with about 2 g. of microcosmic salt (sodium ammonium hydrogen phosphate) and well stirred; about one-fifth the volume of strong ammonia is then added, the mixture vigorously stirred and allowed to stand in the cold for at least four hours and preferably overnight, particularly if the quantity of magnesium is small. The precipitate of magnesium ammonium phosphate is filtered off and washed several times with cold dilute ammonia (1 : 10). It is then redissolved in a minimum quantity of hot dilute (1 : 5) nitric acid, collected in the beaker used for the first precipitation and reprecipitated as follows:—The slightly acid solution is treated in the cold with dilute ammonia until slightly ammoniacal, then a few drops of concentrated microcosmic salt solution are added with vigorous stirring until a precipitate begins to form; after about ten minutes, one-fifth of the volume of strong ammonia is gradually added with constant stirring and the mixture is allowed to stand in the cold for three to six hours, or longer. The precipitate is then filtered off, washed with cold dilute (1 : 10) ammonia until free from chlorides, and eventually ignited to magnesium pyrophosphate, weighed and calculated to magnesia (the conversion factor being 0·3621). The filtrates and washings from the magnesium precipitates are rejected.

The second magnesium ammonium phosphate precipitate can be collected in a Gooch crucible or on a filter paper. The use of the former obviates the troublesome removal of carbon during ignition (see below), but filter paper must be used if it is desired to check the purity of the magnesium pyrophosphate. This nearly always contains traces of calcium phosphate, and possibly of silica and the phosphates of aluminium and manganese, which in the *most* exact work are determined[2] and their combined weight subtracted from the weight of the impure magnesium pyrophosphate. The calcium and manganese impurities are usually due to incomplete separation earlier in the analysis, and the results for lime and manganese oxide can be corrected accordingly. The silica and alumina, if insignificant, are usually due to impurities from the reagents or reagent bottles and therefore their weights are not added to the earlier silica and alumina results.

If a filter paper is used for the collection of the final magnesium ammonium phosphate precipitate, the ignition of the filter and precipitate should be made at as low a temperature as possible in a closed

[1] Simpson, *Ind. Eng. Chem.*, 1921, 13, 1152.

[2] For methods see Mellor, *Quantitative Inorganic Analysis*, 1913, p. 221; and Hillebrand, *Bulletin* 700, *U.S. Geol. Survey*, 1919, p. 152.

crucible and not heated on blast until quite white, otherwise a hard grey mass will result.

Alternative Procedure. When time is important, all the above constituents except silica can be determined in a sample decomposed by hydrofluoric and sulphuric acids as described on p. 225. The particular procedure to be adopted depends upon requirements, one procedure for the analysis of a colourless bottle glass containing as minor constituents small amounts of arsenic, alumina and oxides of iron and manganese being as follows :—

2·5 g. of glass is decomposed with hydrofluoric and sulphuric acids, 0·5 to 1 c.c. of concentrated nitric acid being added with the hydrofluoric acid to prevent loss of any trivalent arsenic during the subsequent evaporation. The hydrochloric acid solution of the residue (see p. 226) is made up to 250 c.c., and from this, 50 c.c. (0·5 g. sample) is withdrawn and used for the colorimetric determination of iron oxide (see below). Arsenic, alumina plus iron oxide, and manganese are in turn precipitated and determined in the remaining 200 c.c. (2 g. sample) and lime and magnesia in half the filtrate from the manganese precipitate (1 g.). The methods given above are employed, except that in this case the arsenic precipitation is quantitative and can be used for the determination of arsenic as described below. It is advisable to make double precipitations, but where speed is very important single precipitations are made and the absence of large quantities of sodium chloride, such as are present in solution when the sample is decomposed by fusion with sodium carbonate, is therefore an advantage.

Lundell and Knowles[1] suggest a procedure somewhat similar to the above, but decompose the sample with hydrofluoric acid and perchloric acid.

Oxides of Sodium and Potassium are determined on a separate sample of glass (0·5 g.) decomposed by calcium carbonate (3 g.) and ammonium chloride (0·5 g.) as in the Lawrence Smith method, or by hydrofluoric and sulphuric acids (see p. 225) as in the Berzelius method. In either case, the alkalis are eventually obtained together as chlorides and weighed as such, the potassium then being separated as chloroplatinate or perchlorate and determined, and the sodium estimated by difference. It is now customary to determine the combined alkalis in a glass by the Lawrence Smith method, and the potassium by the perchlorate method, according to the procedures described for "Clays, etc.," p. 9. To ensure complete decomposition of the sample and avoid low results with the Lawrence Smith method, it is essential to grind the powdered glass, the calcium carbonate, and the ammonium chloride very intimately together, and this is best

[1] *J. Amer. Ceram. Soc.*, 1927, **10**, 829.

achieved by thoroughly grinding together at one time only, say one-fifth of each of the total quantities of the three materials used.

Minor Constituents

Arsenic is frequently, though not invariably, found in glass partly as the pentoxide and partly as the trioxide; when present the whole is usually determined and reported as the pentoxide.

For the total arsenic determination, a sample of glass (2 to 3 g.) is decomposed with hydrofluoric and sulphuric acids in the presence of 0·5 to 1 c.c. strong nitric acid (see p. 225), evaporated almost to dryness, the resulting residue dissolved in dilute hydrochloric acid, and the arsenic removed from that solution by distillation with ferrous sulphate and hydrochloric acid (*cf.* Vol. II., pp. 15, 265) or by precipitation with hydrogen sulphide. In the former case, the arsenic is determined in the distillate by titration with iodine, after neutralising the acid present with sodium bicarbonate, as in Mohr's method (see p. 168), and in the latter, the sulphide precipitate is either dissolved in ammonia and oxidised with hydrogen peroxide[1] or in hydrochloric acid with potassium chlorate by gentle boiling under a reflux condenser, and then the arsenic is either precipitated with magnesia mixture (55 g. anhydrous magnesium chloride, 30 g. ammonium chloride, 5 c.c. strong ammonia and water to 1 litre) and weighed as magnesium pyroarsenate[2] or reduced with hydriodic acid and titrated with iodine, as in Gooch and Browning's modification[3] of Mohr's method.

Allen and Zies[1] have critically investigated the condition of arsenic in glass and the methods of determining it. According to their procedure, 1 g. glass is fused with 3 g. sodium carbonate and 0·1 g. potassium nitrate, the resulting melt being treated with dilute sulphuric acid, evaporated until the nitric acid is driven off and fumes of sulphuric acid are evolved, then cooled, diluted, filtered to remove silica and the arsenic precipitated in the filtrate by hydrogen sulphide; the arsenious sulphide precipitate is used for the gravimetric or volumetric determination of arsenic as above. Allen and Zies state that the volumetric (iodine) method is more accurate than the gravimetric method, and therefore is to be preferred for determining small amounts, and they give details of the best procedure for that method.

When glass is decomposed by hydrofluoric and sulphuric acids in the absence of an oxidising agent, all the trivalent arsenic present, according to Allen and Zies,[1] is lost by volatilisation as arsenic trifluoride, but all the pentavalent arsenic remains in the residue.

[1] Allen and Zies, *J. Amer. Ceram. Soc.*, 1918, **1**, 739.

[2] Levol's Method; see Austin, *Amer. J. Sci.*, 1900, [4], **9**, 55.

[3] Gooch and Browning, *Amer. J. Sci.*, 1890, **3**, 40 and 66; Washburn, *J. Amer. Chem. Soc.*, 1908, **30**, 31.

Trivalent arsenic, therefore, can be estimated by difference if the total arsenic is determined on one sample and the pentavalent arsenic on another, which is decomposed by hydrofluoric and sulphuric acids in the absence of an oxidising agent. It is advisable to use the volumetric method for each determination.

Antimony occurs less frequently in glass than arsenic. When determined, it is usually reported as antimony trioxide. The antimony in a sample of glass is separated as sulphide by methods similar to those described above for arsenious sulphide. For exact work, the antimony sulphide is dissolved with hydrochloric acid and a small amount of potassium chlorate and the antimony is then determined volumetrically by one of the standard methods,[1] such as, reduction with hydriodic acid followed by titration of the iodine liberated with standard sodium thiosulphate (Weller's method), or reduction with sodium sulphite followed by titration of the trivalent antimony with standard iodine solution (Mohr's method), or with standard potassium bromate solution (Gyory's method). For less exact work, the antimony sulphide may be weighed as such or converted to oxide and weighed.

Arsenic and antimony are occasionally, but very rarely, found together in glass. When both have to be determined, the methods given above for arsenic are modified as follows:—(*a*) If the distillation method is adopted the arsenic is removed and collected in the portion distilling at 100° to 110°. Zinc chloride is added to the residue, the temperature raised to 180° and the antimony distilled off[2] and collected separately (*cf.* Vol. II., pp. 15, 265). Arsenic is determined by titration in the first distillate and antimony in the second. (*b*) If the two are precipitated together as sulphides, arsenic is subsequently separated by precipitation with magnesia mixture in the presence of tartaric acid and finally weighed as magnesium pyro-arsenate, and antimony is precipitated as sulphide in the filtrate from the arsenic, the sulphide precipitate being used for the determination of antimony as outlined above.

Iron occurs in all glasses and is generally present mostly in the ferric, but partly in the ferrous state.[3] Except for special purposes, the total iron is determined and reported as ferric oxide. This determination is important for controlling the manufacture of colourless glass and is usually carried out on a separate sample for greater speed and in order to simplify the "blank" determination with the reagents. Two g. is decomposed with hydrofluoric and sulphuric acids and 2 c.c. nitric acid (to oxidise all the iron to the ferric state), evaporated almost to dryness (see p. 226), and the resulting residue dissolved in

[1] See Mellor, *A Treatise on Quantitative Inorganic Analysis*, 1913, pp. 299-304.
[2] Gibbs, *J. Soc. Chem. Ind.*, 1901, p. 184.
[3] Ferguson and Hostetter, *J. Amer. Ceram. Soc.*, 1919, **2**, 608.

5 c.c. concentrated hydrochloric acid and about 100 c.c. hot water with gentle boiling. The solution is cooled, made up to 500 c.c. and the iron determined colorimetrically as described on p. 171. An accurate "blank" determination is made on the reagents employed and a correction applied if necessary.

Ferguson and Hostetter[1] have described methods for the rapid electrometric determination of iron in some optical glasses. They give full details for decomposing the glass, for obtaining in solution the iron in the glass, and for determining the total iron by titration with potassium dichromate after reduction with stannous chloride, using the electrometric method for the determination of the end-point. The method is to be recommended for repetition work, because when the necessary apparatus (*cf.* Vol. II., p. 25) is once collected and fitted up determinations can be made very rapidly, and, by a suitable modification, both the ferrous and ferric iron can be determined in the same sample (see p. 177).

Manganese, when present in glass, usually occurs partly in the trivalent and partly in the divalent condition. The total manganese is determined and generally reported as Mn_3O_4. For its determination, the manganese is obtained in solution, oxidised to permanganic acid and then determined colorimetrically or volumetrically, the methods employed being similar to those for determining manganese in steels and non-ferrous alloys (see Vol. II., pp. 55-57).

A sample of glass is decomposed with hydrofluoric and sulphuric acids as described on p. 225, and the residue treated by either of the following methods to convert any manganese present into permanganic acid:—(*a*) The residue is boiled with about 100 c.c. chlorine-free nitric acid (sp. gr. 1·14) until completely dissolved and then cooled by placing the beaker containing it in ice-water. About 1·5 g. of sodium bismuthate is added, the solution gently shaken for a few minutes and the beaker then stood in a cool place until the excess sodium bismuthate has settled. The pink permanganic acid solution is filtered through a large Gooch crucible, the residue being washed by decantation with 3 per cent. nitric acid.[2] (*b*) Alternatively, the residue is taken up with dilute chlorine-free nitric or sulphuric acid and the manganese present oxidised to permanganic acid by means of ammonium persulphate in the presence of silver nitrate,[3] as described

[1] *J. Amer. Ceram. Soc.*, 1919, 2, 608.

[2] For details of the bismuthate method, see Vol. II., p. 56; Arnold and Ibbotson, *Steel-Works Analysis*, 1907, p. 90; Blair, *The Chemical Analysis of Iron*, 1918, p. 116; Ibbotson, *The Chemical Analysis of Steel-Works Materials*, 1920, p. 81.

[3] For details of the persulphate method, see Mellor, *A Treatise on Quantitative Inorganic Analysis*, 1913, p. 382; Blair, *The Chemical Analysis of Iron*, 1918; Hillebrand, *Bulletin* 700, *U.S. Geol. Survey*, 1919, p. 137; or Ibbotson, *The Chemical Analysis of Steel-Works Materials*, 1920.

under Clays, etc. (p. 7). In either case, the manganese in the sample is obtained as a permanganic acid solution and it is then determined colorimetrically or volumetrically. If the colorimetric method is used, 1 g. of sample is taken and 2 g. or more if the volumetric method is employed.

Sulphur Trioxide.—All glasses made in tank furnaces contain at least a trace of sulphur trioxide due either to the presence of saltcake in the batch or of sulphur in the furnace gases. Gelstharp[1] found that samples of plate glass made from a batch in which saltcake was present contained sodium sulphate in solution in amounts varying from 0·59 to 1·74 per cent. The solubility of sodium sulphate in glass is limited and depends upon the composition of the glass. "Milkiness" in bottle glass has occasionally been caused by the glass being supersaturated with sodium sulphate. The determination of sulphur trioxide in glass is therefore necessary for certain technical investigations and for complete analyses.

For the determination, a sample of glass is decomposed by fusion with sodium carbonate and the sulphate precipitated without removal of the silica, as described under Clay, etc., p. 15. If possible, electrical heating should be employed for this fusion, but if a gas flame has to be used, precautions should be taken to prevent the burner gases from passing into the crucible. To exclude flame gases from the crucible during a fusion, Hillebrand[2] recommends the use of a perforated disc of stiff platinum foil, suitable in size for the crucible being used and having an opening to admit the crucible to about two-thirds of its depth. The disc may be used alone upon the ring of an ordinary (retort) stand or in combination with an asbestos board in which is an opening considerably larger than the crucible and which is held in a clamp. The combination should be slightly inclined to allow the products of combustion to flow to one side without the possibility of enveloping the mouth of the crucible. If a platinum disc is not available, a perforated asbestos board alone will yield fair service with a blast, but with an ordinary burner it is difficult to obtain a sufficiently high temperature for complete fusion.

The fused mass is digested with 100 to 150 c.c. of hot water, filtered, the residue washed with hot dilute sodium carbonate solution, and the filtrate and washings collected together and later made slightly acid with hydrochloric acid. To prevent precipitation of silica, the acid must be added to the *cold* filtered solution and only a slight excess used. The solution is then boiled, and to the boiling solution a moderate excess of a 10 per cent. solution of pure barium chloride is slowly added. The mixture is allowed to stand overnight, the barium

[1] *Trans. Amer. Ceram. Soc.*, 1912, 14, 665.
[2] *Bulletin* 700, *U.S. Geol. Survey*, 1919, p. 34.

sulphate then collected by filtration, washed, ignited and weighed. If there is any fear of silica being present, the ignited precipitate (before weighing) is moistened with water, treated with a few drops of hydrofluoric and sulphuric acids, cautiously evaporated to dryness, ignited and weighed. The percentage of sulphur trioxide is calculated from the weight of barium sulphate obtained, the conversion factor being 0·343.

For this determination, the reagents employed should be as free as possible from sulphur. A "blank" determination is carried out with the reagents to check their purity and a correction is applied, if necessary, to the weight of barium sulphate obtained in the glass analysis.

Chlorine.—Sodium chloride is soluble to a limited extent in glass and, therefore, when it is present in a batch, there is a possibility of some of it being present in the resulting glass. Gelstharp[1] reports finding 0·91 and 1·48 per cent. sodium chloride in two samples of plate glass.

To determine chlorine in glass, a finely ground sample is decomposed by fusion with chlorine-free sodium carbonate (see p. 228) at as low a temperature as possible, the resulting melt digested with hot water, filtered and the residue washed with hot water or dilute sodium carbonate solution. The combined filtrate and washings when cold are made slightly acid (compare "Sulphur Trioxide" above) with chlorine-free nitric acid, and chlorine is then determined in the solution either volumetrically (by Volhard's process), gravimetrically as silver chloride, or, if small amounts are to be determined, nephelometrically.[2] If the gravimetric method is used, the purity of the ignited and weighed precipitate is tested by dissolving it in ammonia; any insoluble matter is filtered off, washed, weighed after ignition and the weight subtracted from the weight of the impure silver chloride precipitate. Whichever method is used, a careful "blank" determination is carried out and a correction applied if necessary.

Titania.—As the determination of this constituent is carried out in the solution of the "cake" obtained by the bisulphate (or pyrosulphate) fusion of the ignited alumina, etc., precipitate, the following details about that fusion are given here.

After the final ignition and weighing of the combined alumina, iron oxide and titania (see p. 231), powdered potassium bisulphate or pyrosulphate equal to eight times the weight of the precipitate is added to the (platinum) crucible, mixed with the precipitate by means of a platinum wire and then cautiously fused. The preliminary heating, especially with bisulphate, must be very gradual; the covered crucible

[1] *Trans. Amer. Ceram. Soc.*, 1912, **14**, 665.
[2] Guye, *J. Phys. Chem.*, 1913, **10**, 145; Meyer and Stahler, *Z. anorg. Chem.*, 1913, **77**, 255.

is heated over a small flame until the contents are melted and then it is raised six to nine inches above a (screened) flame and carefully heated until the moisture is driven off. By adjusting the flame carefully, the moisture can be driven off without loss due to spattering, and then the crucible is gradually lowered towards the flame and finally heated until the bottom of the crucible shows dull redness, great care being taken throughout to regulate the rate of heating in such a way as to prevent frothing. If any particles of the precipitate adhere to the sides of the crucible, they should be incorporated in the melt by rotating or inclining the crucible (with tongs) to permit the fused salt to act on the grains. By removing the crucible with tongs and viewing the cooling contents in a good light, it is possible to see if all the precipitate has dissolved. When solution appears to be complete, the crucible is heated for a further few minutes, and then cooled by placing on a cold slab.

Cold water is added to the crucible when the latter is cold, and the cake usually soon becomes loose, when it is transferred, with water, to a small porcelain basin. Eleven to twelve c.c. of sulphuric acid is added and the mixture warmed and stirred until the cake dissolves.

The procedure then depends upon the determinations which it is desired to make, the full procedure being as follows:—The solution of the cake in the porcelain basin is evaporated on a water-bath to a small volume and then heated to a higher temperature until strong fumes of sulphuric acid are evolved. It is then cooled, and when cold, about 40 c.c. of water is added. The porcelain dish is then heated for some time on a water-bath (to ensure the solution of the soluble constituents), after which the residual silica (see p. 231) which separates out is filtered off through a *small* filter paper. The silica precipitate is washed with successive small amounts of warm water until free from sulphates, then dried, ignited and weighed. The weighed silica is treated with a few c.c. of hydrofluoric acid and a few drops of sulphuric acid and evaporated to dryness (see p. 229), then re-ignited and re-weighed, the difference between this weight and the former one representing the weight of pure silica, which is then added to the main silica determined earlier (see p. 230).

The filtrate and washings from the silica precipitate are concentrated (if necessary) to about 90 c.c., cooled, transferred to a 100 c.c. graduated flask and made up to 100 c.c. with distilled water. Twenty c.c. of this solution is withdrawn and transferred to another 100 c.c. graduated flask, there diluted with distilled water to 100 c.c., and the resulting solution used for the colorimetric determination of iron oxide (see p. 171), 10 c.c. or more being used per titration in the examination of colourless glasses, and 5 c.c. with pale green glasses.

The remaining 80 c.c. of the first solution is used for the determina-

tion of titania as follows:—Five c.c. of hydrogen peroxide (20 volumes strength) is added and afterwards sufficient distilled water to make up the bulk to 100 c.c., the whole then being shaken. By following the above procedure, the solution is obtained with the correct sulphuric acid content (about 9 c.c. per 100 c.c. solution) for the colorimetric determination of titania, which is carried out by "matching" the yellow colour produced by the oxidising action of the hydrogen peroxide on the titanium sulphate solution.

Standard titanium sulphate solution may be prepared by digesting 3·1 to 3·2 g. of potassium titanofluoride—K_2TiF_6—in a platinum dish with strong sulphuric acid and evaporating nearly to dryness. The process is repeated three times to ensure complete expulsion of fluorine, the final residue being taken up with a little strong sulphuric acid and water and diluted to 1 litre.

Alternatively, 1 to 1·1 g. of titanium dioxide and 3 g. of ammonium persulphate, well mixed together, are cautiously heated until vigorous action has ceased and then further gently heated until the ammonium salts have been driven off. The residue is heated with 20 c.c. strong sulphuric acid until dense fumes are evolved and the residue dissolved. After cooling, the sulphuric acid solution is poured into about 900 c.c. of water, well stirred to ensure solution of the titanium sulphate and diluted to 1 litre.

Whichever method of preparation is adopted, the strength of the titanium sulphate solution is accurately determined by duplicate gravimetric determinations of titanium dioxide (precipitated with ammonia as described on p. 230). using 50 c.c. or 100 c.c. of solution for each determination. When the exact strength of the solution is known, the quantity of water which it is necessary to add to the remaining solution to dilute it to a strength of 1 g. of titanium dioxide per litre is calculated and then added. The final solution is stored in a glass-stoppered bottle, and 5 c.c. or 10 c.c. of it freshly withdrawn for each set of colorimetric determinations.

A comparison solution is prepared by transferring with a pipette 5 c.c. of the standard titanium solution (containing 1 g. of titanium dioxide per litre) to a 100 c.c. graduated flask, adding 5 c.c. of hydrogen peroxide (20 volumes) and diluting to 100 c.c. This resulting solution contains 0·00005 g. of titanium dioxide per c.c., and it has a stronger yellow colour than the oxidised test solution.

For determination, some of the oxidised test solution is poured into a 60 c.c. or 100 c.c. colorimeter cylinder of the Nessler type. Five c c. of the oxidised standard dilute titanium solution is added to an identical cylinder and then distilled water is run in from a burette, with repeated stirring, until the colours of the solutions in the two cylinders are the same, the volume of water added being noted.

Repeat determinations should be made until concordant results are obtained. If a colorimeter is available, it should be used; otherwise it is often convenient to adjust the volume of test solution in the one cylinder to be equal in height to that of the liquid in the comparison cylinder after each addition of water, so that the colours of the two solutions can be compared both by looking through and down the columns. As according to the above procedure the volume of test solution is small, the portion of it used in each determination should be returned to the 100 c.c. flask after the comparison is complete, and the solution used again for the repeat determination.

The following is an example of the calculation of results:—Say it is necessary to add 40 c.c. of water to 5 c.c. of oxidised dilute titanium solution to make its colour the same as that of the test solution. Then 45 c.c. (40 + 5) test solution contain the same amount of titanium dioxide as 5 c.c. of the dilute standard solution, which is 0·00025 g. Therefore, 100 c.c. or 0·8 g. sample contain $0\cdot00025 \times \frac{100}{45}$ g. titanium dioxide, and its percentage in the sample is $0\cdot00025 \times \frac{100}{45} \times \frac{100}{0\cdot8} = 0\cdot07$ per cent. titanium dioxide approx.

By following the above complete procedure for small amounts of silica, iron oxide and titania, alumina can be determined accurately by difference in the ammonia precipitate.

It should be noted, however, that although titania is usually present, it is very seldom determined in, say, pale green bottle or window glass, or in colourless bottle glass. Further, the amount of titania in such glasses is so small that really accurate results cannot be obtained with a sample so small as 1 g.

Titania has been recommended as a constituent of heat-resisting glasses, and the colorimetric method described above can be successfully used for the determination of up to 3 per cent. of titania in such glasses with a suitable adjustment of solution strengths (say, dilute the test solution from 100 c.c. to 250 c.c., and double the strength of the dilute standard titanium solution), for it should be noted that the above-mentioned solution strengths have been framed to suit ordinary pale green lime-soda glass.

Selenium as a minor constituent in these glasses is seldom determined, but when necessary can be colorimetrically determined as on p. 274.

Routine Analysis

In the methods described above, suitable procedures are indicated where possible for both exact and approximate analyses. For the examination of single or new glasses, complete analyses should be carried out and the methods suitable for exact analyses should

preferably be used. In routine and works' analyses, the permissible limits of accuracy vary widely according to the purpose for which the results are required. Only the most accurate determinations are of any use for certain control purposes, but in these tests partial analyses frequently suffice. On the other hand, approximate analyses are often satisfactory for, say, checking the composition of cullet. Each analyst, therefore, should select from the alternatives given the procedure most suitable for his requirements.

Where speed is essential and where a partial analysis is sufficient, the determination of alkali oxides is frequently omitted, silica is determined on one sample decomposed by sodium carbonate and the basic oxides other than alkali oxides on another sample decomposed by hydrofluoric and sulphuric acids. The exact silica determination is carried out as on p. 228. For an approximate silica determination, only one evaporation to dryness is carried out and the weight of the (impure) first silica precipitate (see p. 229) is taken as the weight of the silica in the sample. For glasses dealt with in this section such an approximate determination is, with careful work, accurate to within about 0·5 per cent. For example, in twenty-five analyses of a bottle glass containing approximately 74·4 per cent. silica, 0·4 per cent. alumina, etc., 8·3 per cent. lime and 16·9 per cent. sodium oxide, working with 1 g. samples the first (impure) silica precipitate weighed on the average 4·0 mg. less than the true weight of silica, the maximum difference being 5·5 mg. and the minimum 3·0 mg. (Cauwood).

Exact and approximate determinations of the bases other than the alkali oxides on a sample decomposed by hydrofluoric and sulphuric acids have been discussed on p. 235. With simple alkali lime-silicate glasses, rapid determinations of the basic oxides, including alkali oxides, can be carried out on a sample decomposed by hydrofluoric and oxalic acids, as in Sullivan and Taylor's method (see p. 258).

2. Boro-silicate Glasses free from Lead and Barium.

The methods given below are employed for the determination in glass of silica, boric oxide, alumina, zinc oxide, lime, magnesia and the oxides of sodium and potassium as major constituents, and the oxides of arsenic, antimony, iron, manganese, titanium and zirconium, chlorine and sulphur trioxide as minor or special constituents. These constituents are present in such glasses as chemically resistant and heat-resisting glasses, and many optical, thermometer and illuminating glasses.

Barium oxide is occasionally a constituent of chemical glassware, for example, the Jena chemical glassware labelled "20," and when this

oxide is present, the analytical procedure has to be modified as described on p. 260.

Silica is determined as described on p. 228. When zinc is present, it is necessary to remove the silica as completely as possible before proceeding to determine basic constituents, in order to obviate the precipitation of a zinc silicate when the solution is made ammoniacal for the precipitation or recovery (as scum) of alumina (see below). If it is intended to use the filtrate from the silica for the determination of the basic oxides other than the alkali oxides, it is necessary to remove the boric oxide during the evaporations to dryness for the silica separation. This is accomplished by adding pure methyl alcohol (about 20 c.c.) to the solution in the evaporating basin during each of the two evaporations (see p. 229), when the bulk has been reduced to about 40 to 50 c.c. Allen and Zies[1] recommend the following alternative procedure:—After the second evaporation for silica, the evaporating basin and contents are cooled, 25 c.c. of pure methyl alcohol partially saturated with hydrochloric acid gas added, and the contents of the basin again evaporated to dryness on the water-bath, the treatment being repeated with a second 25 c.c. of methyl alcohol.

Basic Oxides other than Alkali Oxides are determined either in the filtrate from the silica (boric oxide having been removed as above) or in a separate sample of glass decomposed by hydrofluoric and sulphuric acids.

(*a*) *Zinc-free Glasses.* With such glasses, the methods previously described are employed for the determination of alumina, iron oxide and titania (see p. 230), manganese oxide (p. 232), lime (p. 233) and magnesia (p. 234).

(*b*) *Glasses containing Zinc.* It is not possible to separate zinc and aluminium completely by two precipitations with ammonia if both are present in appreciable quantity and, therefore, the usual analytical procedure must be modified in the case of many glasses containing zinc. Either of the following methods may be adopted.

1. Removal of the alumina before the precipitation of zinc.

Two precipitations with ammonia, carried out as described on p. 230, separate aluminium from zinc sufficiently completely for all except the most exact analyses when the amount of alumina present in the glass does not exceed 1 per cent. For very exact work, however, and where the alumina content is appreciable, the alumina, iron oxide and titania should be separated from the zinc by the basic acetate process. As sulphates interfere with this process, it is carried out on the sample taken for the silica determination, the procedure being as follows:—

After the removal of silica and boric oxide (see above) arsenic and

[1] *J. Amer. Ceram. Soc.*, 1918, 1, 739.

antimony, if present, are precipitated by means of hydrogen sulphide and removed by filtration. The precipitate, after washing, is rejected. The filtrate is boiled until all the hydrogen sulphide is expelled, then concentrated by evaporation to about 150 c.c. after the addition of 1 c.c. strong nitric acid to oxidise the iron present, and then cooled.

If arsenic and antimony are absent, the filtrate from the silica is simply oxidised, concentrated by evaporation (if necessary) to about 150 c.c. and cooled.

The basic acetate separation is carried out as follows. A strong solution of sodium carbonate is added drop by drop from a burette with constant stirring to the 150 c.c. of cold solution (obtained as above) until the precipitate formed by the addition of the sodium carbonate dissolves only with difficulty upon stirring. A dilute solution of sodium carbonate is then added, drop by drop, until a slight turbidity is attained which persists after vigorous stirring for one to two minutes. One c.c. of acetic acid of sp. gr. 1·044 (33⅓ per cent.) is then added and the solution well stirred. If the solution is not clear after two minutes, more acetic acid is added one drop at a time, with vigorous stirring, until the turbidity just disappears, but an excess of acid must be avoided.

After the above neutralisation process has been carried out, 2 g. of sodium acetate dissolved in a small amount of hot water is poured into the solution, and sufficient boiling water added to make the total volume about 400 c.c. The solution is then immediately heated to boiling point and boiled for one minute, after which the precipitate is allowed to settle and then filtered off as rapidly as possible. Prolonged boiling causes the precipitate to become slimy and very difficult to filter so that there is some risk of the alumina passing into solution again.

The precipitate, which contains the iron, aluminium and titanium present in the sample, is washed with hot 5 per cent. sodium acetate solution, and if bulky it may advantageously be sucked dry at the pump. The precipitate is always contaminated with alkali salts, and is therefore dissolved in hot dilute hydrochloric acid and the metals reprecipitated with ammonia in the presence of ammonium chloride, filtered off and washed in the usual manner (see p. 230).

For very accurate work, the reprecipitation with ammonia should be repeated.

The filtrates from the acetate and ammonia precipitates are combined, made slightly acid with hydrochloric acid, evaporated to 200 to 250 c.c., then made slightly ammoniacal, boiled, and the last traces of alumina, etc., are thus recovered, filtered off and washed.

The final precipitates of alumina, etc., are placed in a platinum crucible together, dried, ignited and weighed, as described on p 231,

and then examined for iron oxide and (if desired) for titania in the usual way (see p. 240).

Zinc is precipitated in the filtrate from the alumina. If manganese is absent, zinc sulphide may be precipitated in ammoniacal solution by the method described (on p. 232) for the precipitation of manganese sulphide. When manganese is present, the solution is neutralised with formic acid, about 3 c.c. excess acid (sp. gr. 1·2) added per 100 c.c. of solution and the zinc precipitated by means of hydrogen sulphide.[1] For the precipitation, the solution is transferred to a small flask, warmed to 50° to 60°, hydrogen sulphide gas passed in until precipitation is complete and the precipitate coagulated (about one hour). The flask is then corked and stood aside in a warm place for some time, preferably overnight. The zinc sulphide is filtered off and washed with hydrogen sulphide water. The washings are collected in separate beakers, as they are sometimes turbid when nearly all the ammonium salts have been washed out of the precipitate, and consequently have to be refiltered. The clear filtrate and washings are combined, made ammoniacal and manganese precipitated and dealt with as described on p. 232.

The zinc sulphide precipitate, however obtained, is dissolved in hot dilute hydrochloric acid and the hydrogen sulphide boiled off. The zinc is precipitated and prepared for weighing by either of the following methods :—

(i) The solution is neutralised with ammonia, then made faintly acid with hydrochloric acid, heated to boiling, and ammonium phosphate added equal to 15 to 20 times the weight of zinc present. The beaker containing the solution (which should then be faintly ammoniacal) is placed on the water-bath until the precipitate of zinc ammonium phosphate becomes crystalline and settles. The precipitate is filtered through a Gooch crucible fitted with asbestos, washed with hot 1 per cent. ammonium phosphate solution until free from chlorides, and finally with alcohol, dried at 100° to 105° and (*a*) weighed as zinc ammonium phosphate (the factor for conversion to zinc oxide being 0·456), or (*b*) ignited by placing the Gooch crucible inside a large porcelain crucible and heating with a Méker or Teclu burner, cooled and weighed as zinc pyrophosphate (the conversion factor to zinc oxide being 0·534).

(ii) Alternatively, the zinc is reprecipitated by sodium carbonate in a very slightly alkaline solution, filtered through a Gooch crucible fitted with asbestos, washed, dried, ignited by placing the Gooch crucible inside a large porcelain crucible and heating with a strong Bunsen burner, cooled and weighed as zinc oxide.[2]

[1] Waring, *J. Amer. Chem. Soc.*, 1904, **26**, 4.
[2] Treadwell and Hall, *Analytical Chemistry*, II., 1919, p. 142.

After the separation of zinc (and manganese if present) the methods previously described are employed for the separation and determination of lime (see p. 233) and magnesia (p. 234).

2. Removal of the zinc before precipitation of alumina.

This procedure is recommended by Allen and Zies[1] and is carried out by precipitating the zinc with hydrogen sulphide in formic acid solution as described above. One advantage of this procedure is that it can be carried out either in the filtrate from the silica (if the glass sample has been decomposed by fusion with sodium carbonate) or in the solution of the residue resulting from the decomposition of a sample of glass with hydrofluoric and sulphuric acids (see p. 225).

The separation of the zinc is carried out as follows:—(*a*) If the glass under examination is free from arsenic and antimony, the solution containing the basic constituents of the glass is neutralised, about 3 c.c. formic acid (sp. gr. 1·2) added per 100 c.c. and the zinc then precipitated with hydrogen sulphide, filtered off and washed, the operations being conducted as described above. (*b*) If arsenic is present but antimony absent, the same procedure is followed and the sulphides of zinc and arsenic are precipitated together, filtered off and washed (see above). The funnel is covered with a suitable clock-glass and the zinc sulphide dissolved by cautiously pouring under the cover a little 1 : 1 hydrochloric acid, the filtrate being collected in a beaker. The filter is thoroughly washed with hot water and the arsenious sulphide then dissolved by pouring a few c.c. of colourless ammonium sulphide directly on the filter and washing into a separate beaker. Traces of zinc sulphide may be left on the filter which, therefore, is treated again with further small quantities of hot dilute hydrochloric acid and washed with hot water, the filtrate and washing being added to the first zinc filtrate. (*c*) When the glass contains antimony, precipitation with hydrogen sulphide is first carried out in a hydrochloric acid solution (4 to 5 c.c. of acid, sp. gr. 1·12 being present per 100 c.c. solution) to remove the antimony (and also arsenic if present), and zinc sulphide is precipitated in the filtrate from the antimony after boiling off the hydrogen sulphide, neutralising and adding the prescribed amount of formic acid (see above, p. 247). After separation, the zinc is determined by either of the methods given above.

The filtrate from the zinc sulphide precipitate is reserved for the determination of alumina, iron oxide and titania, manganese, lime and magnesia by the methods already described (see p. 230 *et seq.*).

Alkali Oxides are determined by the Lawrence Smith method or by the Berzelius method (see p. 235), the former being the more satisfactory. Mellor[2] states that in the Smith process "boron remains

[1] *J. Amer. Ceram. Soc.*, 1918, **1**, 739.

[2] *A Treatise on Quantitative Inorganic Analysis*, 1913, p. 226.

behind as insoluble calcium borate" when the "cake" is digested with water. Allen and Zies,[1] however, recommend that the residue of ammonium and alkali chlorides obtained by evaporation in the Smith process be evaporated to dryness on the water-bath (with the dish covered) with 10 c.c. pure methyl alcohol to ensure complete absence of boric oxide from the final residue of alkali chlorides.

Boric Oxide is determined in a separate sample decomposed by fusion with sodium carbonate. The weight of the sample employed depends on the amount of boric oxide present, and a rough approximation of the boric oxide content can be made by means of the qualitative tests described on p. 222 if repeated tests are carried out with varying amounts of sample. Usually 0·5 g. of finely ground glass sample is weighed out in a platinum crucible, fused with 3 g. sodium carbonate and the fusion stopped about two minutes after the mass becomes liquid, to prevent loss of boric oxide by volatilisation. If the amount of boric oxide in the glass exceeds 10 per cent., there is a great danger of loss of boric oxide in this way and, to obviate this loss, Dimbleby and Turner[2] recommend that with such glasses the weight of sample taken should be reduced to an amount which contains less than 0·05 g. boric oxide, finely ground pure silica added to give a total weight of 0·5 g. of sample fused, and the mixture decomposed with 3 g. sodium carbonate as above. If the glass under examination contains less than 0·5 per cent. boric oxide, 1 g. of glass sample should be taken and decomposed with 4 to 5 g. sodium carbonate. In all cases, the cake obtained by the fusion is used for the determination of boric oxide by one of the following methods:—

(*a*) *Distillation Method.* After testing the various methods used for the determination of boric oxide in glass, Allen and Zies[1] came to the conclusion that the distillation method should be used when great accuracy is desired and when small amounts have to be determined.

For this method, the cake obtained by the fusion of the glass with sodium carbonate is transferred to a 250 c.c. round-bottomed flask (the "decomposition flask") with not more than 50 c.c. hot water. Sufficient strong hydrochloric acid is added to neutralise the sodium carbonate and to give a slight excess of acid, the "decomposition flask" connected to a reflux condenser and the contents boiled to complete the decomposition and expel carbon dioxide. After washing down the reflux condenser with a little water, the flask is disconnected, pure granular anhydrous calcium chloride added (about 1 g. per c.c. of solution), and mixed with the solution by twirling the flask. The "decomposition flask" is then connected to the rest of the distillation

[1] *J. Amer. Ceram. Soc.*, 1918, 1, 739.
[2] *J. Soc. Glass Tech.*, 1923, 7, 76.

apparatus (see Fig. 43) which is similar to that used for steam distillations. It consists of:—a "boiler," A, usually a distillation flask, fitted with a cork carrying a safety trap and containing methyl alcohol and a capillary boiling tube. The "decomposition flask," B, fitted with a two-holed cork, through one hole of which passes a long glass tube with its bottom end below the surface of the solution in the flask, and its top end connected to the delivery tube of the "boiler," and through the other passes a short bent glass tube which is connected with a glass condenser, C, and a conical receiving flask, D, of 250 c.c. capacity fitted with a two-holed cork, through one hole of which passes the bottom end of the inner tube of the condenser or an adapter connected to

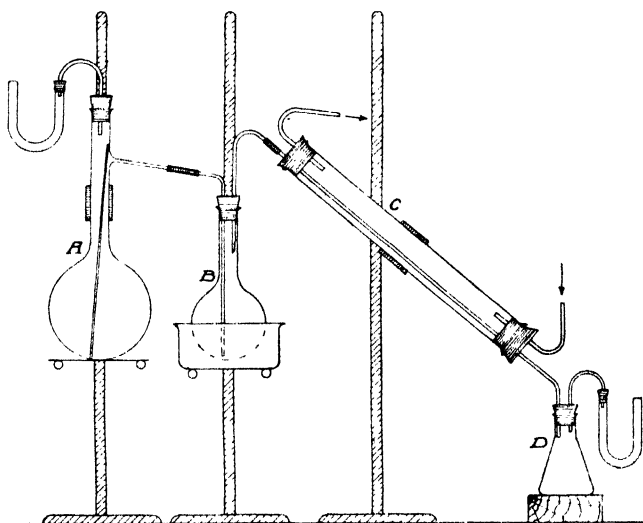



Fig. 43.

the condenser, and through the other hole passes a short bent glass tube connected to a U-tube containing some water to act as a trap. Three or four receiving flasks should be available.

After connecting up the apparatus, distillation of methyl alcohol from the "boiler" is commenced, and when about 25 c.c. has condensed in the "decomposition flask," the latter is heated by means of a water-bath to keep the flask hot enough to prevent further condensation of alcohol. Distillation from the "boiler" is continued and methyl alcohol and methyl borate are slowly distilled off from the "decomposition flask." When about 100 c.c. of distillate has been collected, the receiving flask is changed for a fresh one and a second distillate collected. Meanwhile the contents of the trap U-tube are added to those of the first receiver and the whole treated as follows:—The hydrochloric acid present is just neutralised by the addition of $N/2$ sodium hydroxide, using a

drop of *p*-nitrophenol solution as indicator. Phenolphthalein solution (1 c.c.) is then added and the titration continued until the appearance of a permanent pink colour shows that the boric acid in the solution is approximately neutralised. A further quantity of *N*/2 sodium hydroxide is then added (equal to twice the amount used in the latter titration) to prevent loss of boric oxide in the subsequent distillation, and the solution reserved for further treatment. The second 100 c.c. of distillate is treated in the same manner. If this titration shows that the amount of boric oxide is not appreciable (as is usually the case), the distillation is stopped, but if more than 0·2 c.c. of *N*/2 sodium hydroxide is required in the boric oxide titration, a further 100 c.c. of distillate should be collected and treated similarly.

When the distillation is complete, the treated distillates are combined by transference to a round-bottomed flask (using as little wash water as possible in the process), and the methyl alcohol distilled off, a capillary boiling tube being present to prevent "bumping." (The methyl alcohol is collected and can be recovered for further use by redistillation from quicklime and 100 c.c. strong sodium hydroxide solution.) The residue left in the flask after the complete removal of methyl alcohol is diluted to 25 c.c. (if necessary) and 1 : 1 hydrochloric acid is added drop by drop until the colour of both indicators is just discharged. The flask is then connected to a reflux condenser, the contents gently boiled for five minutes and, after washing down the condenser, the flask is connected to a suction pump through a splash trap and suction applied until boiling ceases (to ensure complete removal of carbon dioxide). When cold, the boric oxide in the solution is titrated with standard sodium or barium hydroxide (*N*/10 or *N*/5), the alkali solution being standardised by means of pure fused boric oxide or pure crystal borax. The titration is carried out by the double indicator method described on p. 140 for the determination of boric oxide in borax, the indicators being *p*-nitrophenol and phenolphthalein, the latter in the presence of mannitol or glycerin. For accurate work, a blank test is carried out using the same quantities of reagents, and the result (usually about 1 mg.) is applied as a correction.[1] Allen and Zies[2] confirm that the method is trustworthy in the presence of small quantities of fluorides and of arsenious oxide, but if much trivalent arsenic is present it must be oxidised to the pentalent condition by hydrogen peroxide in a solution made alkaline with sodium hydroxide before carrying out the distillation. Only pure methyl alcohol can be used for the determination, commercial wood alcohol giving unsatisfactory results.

[1] For further details of the "Distillation Method," see Wherry and Chapin, *J. Amer. Chem. Soc.*, 1908, **30**, 1687 ; Mellor, *A Treatise on Quantitative Inorganic Analysis*, 1913, p. 585 ; or Hillebrand, *Bulletin* 700, *U.S. Geol. Survey*, 1919, p. 235. [2] *J. Amer. Ceram. Soc.*, 1918, **1**, 739.

(*b*) *Wherry's Method* is less accurate than the distillation method, but is very useful for single or approximate analyses. In this method, if zinc and lead are absent, the cake obtained by the fusion of the glass sample with sodium carbonate (see above) is transferred to a 250 c.c. round-bottomed flask with about 40 c.c. hot water and warmed to decompose and soften. A slight excess of strong hydrochloric acid and a few drops of strong nitric acid are added and the solution boiled under a reflux condenser until decomposition is complete. A moderate excess of calcium carbonate is then gradually added and the mixture boiled vigorously for ten minutes, again under the reflux condenser. After the precipitate has settled, the clear solution is filtered under gentle suction through a large Gooch crucible. The precipitate is washed by successively boiling it up with three small quantities of water (under reflux conditions) then transferred to the Gooch crucible, washed under suction with a little hot water, and finally *sucked dry.* The combined filtrate and washings, which together should not exceed 100 c.c., are returned to the round-bottomed flask, about 1 g. of calcium carbonate added and the mixture boiled for ten minutes under the reflux condenser. If a reddish precipitate forms, the mixture is filtered as before and, when cool, the filtrate titrated for boric oxide. If no coloured precipitate forms, the second filtration is omitted, and the flask is connected to a suction pump, with gentle suction at first, through a splash trap until boiling ceases. The solution is then cooled to room temperature and the boric oxide titrated with $N/10$ sodium hydroxide, using phenolphthalein as indicator in the presence of excess of mannitol or glycerin (see p. 140).

In the method described above, silica, alumina, and iron oxide are removed by precipitation with calcium carbonate and a solution is obtained in which the boric oxide can be quickly determined by titration. There are, however, certain drawbacks to the method. The first is that the accuracy of the results is affected by the fact that the precipitates obtained with calcium carbonate carry down some of the boric oxide. By following the procedure described above, this trouble is reduced to a minimum, but for accurate work the precipitates are redissolved together in hydrochloric acid, reprecipitated, filtered and the filtrate titrated for boric oxide, the amount found being added to the result obtained by the first titration. The second disadvantage is that calcium carbonate fails to remove completely zinc and lead if present. For glasses containing zinc and lead, a modified method is employed, as follows.

(*c*) *Sullivan and Taylor's Modification of Wherry's Method.* For this method,[1] the cake obtained by the fusion of the glass with sodium

[1] Sullivan and Taylor, *Ind. Eng. Chem.*, 1914, **6**, 897, and *Chem. News*, 1915, **111**, 64; Cauwood and Wilson, *J. Soc. Glass Tech.*, 1918, **2**, 246.

carbonate is transferred to a small Phillip's beaker with 25 to 30 c.c. of water and gently boiled to decompose the mass. When decomposition is complete, the residue is allowed to settle and the solution is filtered under gentle suction through a large Gooch crucible and collected in a small filter flask. The insoluble residue, which contains any zinc and lead present, is washed by decantation by boiling up three times with a little distilled water, then transferred to the Gooch crucible and washed under suction, being finally sucked dry. The filtrate and washings are transferred to a 250 c.c. round-bottomed flask, a slight excess of hydrochloric acid added, and the procedure is then exactly as described above for Wherry's method for zinc and lead-free glasses. The accuracy of results obtained by this modified method is quite good but is affected, as with the original method, by the retention of boric oxide by the precipitates. Therefore, for accurate work the precipitates are redissolved, reprecipitated, filtered and the filtrates titrated for boric oxide.

A method similar in principle to that described above has been advanced by Nicolardot and Boudet[1] in which silica and bases which interfere with boric oxide titrations are removed in one precipitate. The authors claim that the method gives satisfactory results and they describe all the necessary working details.

(*d*) *Colorimetric Method.* For the determination of small amounts of boric oxide, say, 2 mg. and less, the colorimetric method embodying the use of turmeric paper, described by Bertrand and Agulhon[2] may be employed.

Minor Constituents.—The methods described on pp. 236 to 243 can be employed for the determination of chlorine, sulphur trioxide and the oxides of arsenic, antimony, titanium, iron and manganese occurring as minor constituents in boro-silicate glasses free from lead and barium.

Antimony Oxide is present in a number of boro-silicate chemically-resistant and heat-resisting glasses in amounts varying from 1 to 3·5 per cent., and in certain optical glasses to the extent of about 3 per cent. In such glasses, antimony oxide is rather more than a minor constituent, but nevertheless its determination is carried out by the method described on p. 237 on a sample decomposed with hydrofluoric and sulphuric acids.

The silica determination is, however, affected by the presence of antimony oxide in the quantities stated above, because even if the silica is repeatedly washed by boiling with dilute hydrochloric acid containing tartaric acid, it is almost impossible to free it from antimony; so that there is a large residue left after treating the weighed, impure silica with hydrofluoric acid (p. 230).

[1] *Bull. Soc. Chim.*, 1917, **21**, 97. [2] *Comptes rend.*, 1913, **157**, 1433.

When the quantity of antimony oxide is, say, about 1 per cent., it is customary to carry out the silica determination in the usual manner (p. 228), recognise the fact that the silica precipitate will contain antimony oxide and treat the weighed, impure silica with hydrofluoric and nitric acids, and subtract the weight of the residue (largely antimony oxide) so obtained from the weight of the impure silica to obtain the true weight of silica.

When the antimony oxide content is appreciably higher, say 3 per cent. or more, the following procedure has been recommended by Adam :—Silica is separated from a sample decomposed with sodium carbonate by two evaporations, in the usual way (p. 229). The still moist and impure silica is washed from the filter papers into a platinum basin, the residues adhering to the papers being removed by washing with hot sodium carbonate solution and finally with hot water. A 10 per cent. sodium carbonate solution is then added to the platinum basin in such quantity that 15 to 16 c.c. is present for each 0·1 g. silica, and the solution boiled until the silica is completely dissolved. The platinum basin is then covered with a clock-glass, hydrochloric acid is added from a pipette until the solution is distinctly acid and the silica is then recovered by two evaporations in the usual way, when it is obtained in a pure state, as the antimony oxide previously mixed with the silica passes into the filtrate as chloride.

Titania has, in recent years, been recommended as a special major constituent of heat-resisting glasses, and if found as such, it can be determined as follows :—

(*a*) When present in quantities less than 3 per cent., titania can be determined colorimetrically as described on p. 242, by suitably adjusting solution strengths. (The colorimetric process is accurate over a range of concentrations varying from 0·0015 to 0·02 g. titania per 100 c.c. of test solution.)

(*b*) When present in quantities greater than 3 per cent., titania is best determined gravimetrically as follows :—The titania, alumina and iron oxide present in the sample are precipitated together as in an ordinary analysis (by means of either ammonia or the basic acetate process, according to the procedure adopted ; see p. 245), the precipitate dissolved in warm dilute *hydrochloric* acid, the solution carefully neutralised and the titania precipitated with sulphur dioxide according to Baskerville's method.[1] The titania is filtered off, dissolved in warm dilute *hydrochloric* acid, reprecipitated with sulphur dioxide, again filtered off, washed with hot water, ignited and weighed as titania. (The reprecipitation is to ensure complete separation of iron oxide from the titania.)

[1] See Baskerville, *J. Amer. Chem. Soc.*, 1894, 16, 427, 475 ; Hillebrand, *Bulletin* 700, *U.S. Geol. Survey*, 1919, pp. 130, 166 ; and Dimbleby, *J. Soc. Glass Tech.*, 1927, 11, 161.

In the above process, alumina and iron oxide pass into the filtrates from the titania, in which they can be determined after complete oxidation. When the titania determination is carried out on the sample used for the silica determination, precautions must be taken to prevent the hydrolysis of the titanium salt when washing the silica. Further, if the titania exceeds, say 8 per cent., the glass is very difficult to fuse with sodium carbonate, and hence only 0·5 g. sample should be used for the fusion, instead of the more usual 1 g. Even when all precautions are taken to prevent it, appreciable contamination of the silica with titania takes place with these glasses, and in consequence the residues left after treating the weighed silica with hydrofluoric acid tend to be high; these residues should be fused with a little sodium carbonate and added to the main solution.

Zirconia has recently been found to be a useful special constituent of heat-resisting and chemically-resistant glasses;[1] it is also a constituent of some opal glasses (see pp. 159 and 272). When zirconia is present in a glass (and at the present time it is very seldom found) the analytical procedure is very similar to that employed for titania glasses.

Zirconia is even more troublesome in yielding high residues after treating the silica precipitate with hydrofluoric acid than titania. (These residues must be fused out of the crucible, preferably with sodium bisulphate and added to the main solution.) The heating of the silica for dehydration (p. 229) must be conducted at steam-bath temperature only, and washing must be effected by means of hot dilute hydrochloric acid followed by hot water. If the zirconia content exceeds 5 per cent., only a 0·5 g. sample is used for sodium carbonate fusions.

For determination of zirconia, Baskerville's method is employed, the procedure being as described above for titania, except that in this case the precipitate obtained with sulphur dioxide consists of zirconia plus any titania present. The final weighed and ignited precipitate is fused with sodium bisulphate or pyrosulphate, and the titania determined colorimetrically (as described on p. 242) in the solution of the melt; by subtracting the amount of titania so found from the combined weight of zirconia and titania, the zirconia is obtained by difference. The filtrates from the two zirconia (and titania) precipitates are combined, concentrated, oxidised, and used for the determination of alumina and iron oxide. As a check, it is advisable to determine the combined weight of zirconia, titania, alumina and iron oxide on a separate 0·5 g. sample.

Alternatively, a 1 g. sample can be decomposed with hydrofluoric

[1] See, for instance, Dimbleby and Turner, *J. Soc. Glass Tech.*, 1926, **10**, 324, 326; 1928, **12**, 56.

and sulphuric acids, the residue dissolved in dilute sulphuric acid, filtered if necessary and made up to a suitable bulk. Using aliquot parts of that solution (*a*) titania can be determined colorimetrically on one part as described on p. 242, (*b*) iron oxide can be determined colorimetrically on another part as described on p. 171, and (*c*) zirconia can be determined gravimetrically as zirconium pyrophosphate[1] on a third portion, the acidity of which must be adjusted to 20 per cent. by weight of sulphuric acid.

3. Silicate and Boro-Silicate Glasses containing Lead or Barium, or both.

The analytical procedures discussed in this section apply to glasses containing lead or barium or both in addition to all or some of the constituents mentioned on p. 244. For such glasses, the methods already described are employed for the separation and determination of silica (see p. 228), boric oxide (p. 249), alkali oxides (p. 235), and certain minor constituents, but the procedure for the separation and determination of basic oxides other than alkali oxides is modified as described below.

(a) **Lead Glasses free from Barium.**—Amongst such glasses are "crystal glass" (used for decorative and table-ware), "half-crystal" glass (sometimes used for the cheaper kinds of decorative ware), most electric light globe glasses, and many optical glasses. (Some crystal glasses contain small amounts of phosphates and others small amounts of fluorine, and for such glasses the methods described on p. 261 should be consulted.)

Silica is determined in these glasses by the usual method (see p. 228), but the decomposition of the glass by fusion with sodium carbonate is carried out at as low a temperature as possible and the upper portion of the crucible (covered with a closely-fitting lid) is kept fairly cool to avoid loss of lead by volatilisation. Both silica precipitates are washed with hot water. If lead is to be determined in the same sample as the silica, the residue left after treating the weighed silica with hydrofluoric and sulphuric acids is fused with a little sodium carbonate, dissolved cautiously in the crucible with dilute hydrochloric acid, boiled gently, and transferred (whether wholly soluble or not) to the filtrate from the silica, because the residue usually contains lead. If boric oxide is present in the sample, it is removed during the silica evaporations as described on p. 245.

Basic oxides other than alkali oxides can be determined in the filtrate from the silica as follows:—

Lead Oxide.—The acidity of the solution is adjusted to 3 per cent. by volume of hydrochloric acid (sp. gr. 1·16), the solution boiled

[1] For details see Hillebrand, *Bulletin* 700, *U.S. Geol. Survey*, 1919, p. 173.

and hydrogen sulphide gas then passed into the hot solution for about half an hour. After the precipitate has settled (and preferably after standing two to three hours), the lead sulphide is filtered on a small filter paper, thoroughly washed with warm hydrogen sulphide water and the filtrate and washings reserved (see below). The precipitate is transferred by means of a fine jet of water to a beaker or porcelain basin, dissolved in nitric acid, 3 to 4 c.c. of sulphuric acid (1 : 1) added, the solution cautiously evaporated until copious fumes of sulphuric acid are evolved and then cooled. When cold, the solution is (cautiously) diluted to about 100 c.c., again cooled, preferably in ice water, and allowed to stand for some hours, overnight if possible. The lead sulphate precipitate so obtained is filtered through a Gooch crucible, washed first with cold *N* sulphuric acid and finally with alcohol, the filtrate and acid washings being reserved if the glass contains zinc (see below). After drying at 100°, the Gooch crucible is placed inside a large porcelain crucible, ignited over a Méker flame, cooled and the weight of lead sulphate determined. As it is impossible to wash the lead sulphide completely from the filter on which it is collected, the filter paper is burnt off at a low temperature in a weighed porcelain crucible, the residue evaporated to dryness with a few drops of nitric acid and two drops of sulphuric acid, gently ignited, weighed and the weight of the lead sulphate thus obtained added to that of the main portion. From the final weight of lead sulphate, the amount of lead oxide present in the sample is calculated ($PbSO_4 \times 0{\cdot}736 = PbO$).

Any arsenic present in the filtrate from the silica will be precipitated with the lead sulphide, and if zinc is present, some of it may be precipitated at the same time. The filtrate from the lead sulphate contains any arsenic and zinc present in the lead sulphide precipitate and the zinc (if present) is determined as described on p. 248, the amount found being added to the main portion (determined in the filtrate from the lead sulphide precipitate).

The filtrate from the lead sulphide is used for the determination of alumina, iron oxide and titania, zinc oxide, lime and magnesia as described on p. 245 *et seq.*

Alternative procedures are as follows :—

1. According to the method of Allen and Zies,[1] a sample of glass is decomposed with hydrofluoric and sulphuric acids (see p. 225) and cautiously evaporated until all the hydrofluoric acid is driven off. The pasty mass, after cooling, is transferred to a beaker by a jet of water, diluted to about 150 c.c., boiled and left to stand some hours, preferably overnight. By this procedure the lead present in the sample is separated directly as lead sulphate, which is filtered off and determined as above, the filtrate being used for

[1] *J. Amer. Ceram. Soc.*, 1918, **1**, 739.

the determination of the other basic oxides as described on pp. 245 to 248.

2. As there is some danger of loss by bumping during the decomposition of a heavy lead glass with hydrofluoric and sulphuric acids, some analysts prefer to use hydrofluoric and nitric acids as described on p. 226.

(*a*) If it is necessary or desirable to avoid the presence of sulphuric acid in the filtrate from the lead (as, for example, when an accurate alumina determination is required), the decomposition of the glass sample with hydrofluoric and nitric acids is followed by the usual evaporation to dryness on the water-bath. The residue of nitrates so obtained is dissolved with hot water, transferred to a beaker and diluted to about 200 c.c. (To ensure that the residue is completely transferred to the beaker, the platinum crucible, or dish, used for the decomposition may be finally cleaned out by gently boiling in it a little water containing one or two drops of nitric acid and the washings added to the main solution, but care must be taken not to exceed the amount of nitric acid stated.) Three per cent. by volume of hydrochloric acid (sp. gr. 1·16) is added to the solution of the residue, and lead and basic oxides other than those of sodium and potassium are then separated and determined by the same procedure as that described above for use with the filtrate from the silica.

(*b*) If the presence of sulphuric acid in the filtrate from the lead is not objectionable, the residue of nitrates obtained by the decomposition of the sample with hydrofluoric and nitric acids is dissolved in a small quantity of hot water and a few drops of nitric acid, transferred to a beaker, 3 to 4 c.c. of sulphuric acid (1 : 1) added, and evaporated (cautiously) until strong fumes of sulphuric acid have been evolved for a few minutes. After cooling, the solution is cautiously diluted to 150 c.c., again cooled and then the procedure is exactly the same as with a sample decomposed with hydrofluoric and sulphuric acids (see above).

3. Sullivan and Taylor's Method. This method was first developed for the analysis of glasses which contained varying amounts of silica and the oxides of lead, sodium and potassium, and only traces of other substances. For such glasses, the method is to weigh out 1 g. of sample in a large platinum crucible, moisten it with water, add 2 g. of oxalic acid and about 20 c.c. of 48 per cent. hydrofluoric acid and evaporate to dryness on a radiator, the temperature of which is just high enough to expel the excess of oxalic acid. When the excess acid has been driven off and the crucible cooled, the evaporation is repeated twice with oxalic acid and water. (About 5 g. of oxalic acid are used in all and a blank experiment for alkalis is carried out on this quantity of acid.) After the third evaporation, the remaining

oxalates are taken up with hot water, the solution allowed to cool and filtered. The residue, which in these glasses consists only of lead oxalate with a trace of calcium oxalate, may be titrated directly with potassium permanganate or dissolved in dilute nitric acid and the lead determined as sulphate (as above).

The filtrate from the lead oxalate is evaporated to dryness in a platinum dish and the dry residue heated over a free flame until the oxalates are decomposed. The resulting carbonates are dissolved in dilute hydrochloric acid, evaporated to dryness, taken up with water and filtered to remove the small amount of silica which is usually present. The filtrate from the silica is oxidised by heating with bromine water, and iron, aluminium and manganese are then precipitated together as hydroxides with ammonia. The precipitate is filtered off and the filtrate divided into two equal parts.

In one half magnesia is determined by precipitation with microcosmic salt and ammonia (see p. 234). The percentage of magnesia in the original sample and also the weight of magnesium chloride in the solution are calculated from the weight of the precipitate.

The second half of the solution is evaporated to dryness in a weighed platinum dish, gently ignited to drive off ammonium salts, cooled and weighed. From the weight of mixed chlorides so determined, the correct weight of alkali chlorides derived from the alkali oxides in the glass is obtained by subtracting both the weight of magnesium chloride determined above and the relevant weight determined in the oxalic acid blank experiment. Potassium chloride is determined in the mixed chlorides in the usual way (see p. 235), sodium chloride is then obtained by difference, and the percentages of potassium and sodium oxides in the glass calculated from those results.

Sullivan and Taylor suggest that the method may be capable of application to more complicated types of glass and in their original paper[1] they describe and discuss tests illustrating the possibilities of this.

Both Sullivan and Taylor[1] and Allen and Zies[2] state that the result for lead oxide determined in a sample decomposed with hydrofluoric acid is usually higher than when the determination is made in the filtrate from the silica. Allen and Zies suggest that this is possibly due to the mechanical losses which occur in the more complicated procedure which the latter method necessitates.

Minor Constituents. — The methods already described can be employed for the determination of sulphur trioxide (p. 239) and

[1] "Some Rapid Methods of Glass Analysis," *Ind. Eng. Chem.*, 1914, 6, 897; and *Chem. News*, 1915, 111, 64.

[2] *J. Amer. Ceram. Soc.*, 1918, 1, 739.

chlorine (p. 240). Manganese is determined by the bismuthate method (p. 238) on a sample decomposed by hydrofluoric and nitric acids (p. 226) and iron oxide is determined colorimetrically (p. 171) in a sample decomposed in the same way. With regard to arsenic and antimony, the methods already described (pp. 236 and 237) are employed subject to the following slight modification:—When the sample is decomposed by hydrofluoric and sulphuric acids, the resulting residue should contain 2 to 3 c.c. of strong sulphuric acid and is taken up with water, *boiled* and then allowed to stand in the cold for some hours to ensure complete precipitation of lead sulphate, which is then filtered off and washed. The filtrate contains the arsenic and antimony. Boric oxide sometimes occurs as a minor constituent and, when necessary, it is determined as described on p. 249 or p. 252.

(b) **Barium Glasses free from Lead.**—In this category are certain optical glasses and glasses used for pressed ware.

The analysis of these glasses differs from the analysis of lead glasses free from barium only in that instead of lead oxide, barium oxide has to be determined by precipitation and weighing as barium sulphate. It is advisable, whenever possible, to remove barium from a solution before carrying out precipitations with hydrogen sulphide, ammonia and ammonium sulphide, as such precipitations may cause loss of barium from the solution owing either to oxidation of sulphide to sulphate or to the presence of carbonates and sulphates in the reagents used, and, further, ammonium salts exercise a retarding influence on the precipitation of barium sulphate.

Barium oxide is, therefore, determined by one of the following methods:—

(1) A sample of glass (1 g.) is decomposed by fusion with sodium carbonate, silica is separated and determined in the usual way (p. 228) and the residue left after treating the weighed silica with hydrofluoric and sulphuric acids added to the filtrate from the silica, as described above for lead determinations. The combined solutions (which should be sufficiently dilute to hold in solution as sulphate any calcium present) are raised to boiling, a slight excess of hot dilute sulphuric acid gradually added with constant stirring to precipitate the barium as sulphate, and the mixture allowed to stand in a warm place for several hours, overnight if possible. The barium sulphate is filtered off and washed free from chlorides. The damp paper and precipitate are dried cautiously in a weighed platinum crucible, heated to char the filter paper without flame, and finally ignited to constant weight. The weight of barium sulphate is determined and the weight of barium oxide calculated, the conversion factor being 0·657. The determination is subject to the usual errors of barium sulphate determinations.[1]

[1] See Allen and Johnston, *J. Amer. Chem. Soc.*, 1910, **32**, 604; see also Vol. I., p. 368 *et seq.*

The filtrate from the barium sulphate contains the other basic constituents of the glass and these, other than the alkali oxides, can be determined by the methods described on p. 245 *et seq.*

(2) Alternatively, barium oxide and the other basic oxides (except alkali oxides) present in a glass can be determined on a sample decomposed by hydrofluoric and sulphuric acids as described above for lead glasses. The procedure is the same as for lead glasses except that in this case it is barium sulphate and not lead sulphate which is filtered off, washed, ignited (as above) and weighed.

Minor Constituents.—Determinations of small amounts of sulphur trioxide, chlorine and the oxides of arsenic, antimony, iron and manganese can be made in barium glasses by the same procedure as that employed with lead glasses (p. 259).

(c) **Glasses containing both Lead and Barium.**—Certain optical glasses and a few decorative glasses contain both lead and barium.

The analysis of such glass differs from the analysis of lead glasses free from barium only as regards the determinations of the bases, and for such determinations either of the following procedures may be adopted :—

(*a*) The determinations are carried out on the sample taken for the silica determination. A weighed sample (1 g.) is decomposed by fusion with sodium carbonate, and silica, boric oxide (if present) and lead (as sulphide) are removed by the same procedure as that described (p. 256) for lead glasses free from barium. Barium oxide and the remaining basic constituents of the glass (except alkali oxides) are then determined in the filtrate from the lead sulphide by the procedure outlined above for barium glasses free from lead.

(*b*) Alternatively, silica and lead oxide are determined on one sample decomposed by sodium carbonate (p. 256), while lead and barium are determined together as sulphates on a sample decomposed by hydrofluoric and sulphuric acids. From the results so obtained, barium oxide is estimated by difference. The other basic oxides, except alkali oxides, are determined in the filtrate from the combined lead and barium sulphate precipitate.

4. Transparent Glasses containing Phosphoric Oxide and Fluorine

Phosphoric oxide is present as a major constituent in a few colourless transparent glasses, such as special optical glasses, and as a minor constituent in certain flint glasses. The procedure for the analysis of such glasses is similar to that employed for opal glasses containing phosphoric oxide (p. 266).

Fluorine is present in very few colourless or pale green transparent glasses. It occurs occasionally in crystal glass and (infrequently) in bottle glass, and attempts have been made to introduce it into special

optical glasses. For the analysis of such glasses, the procedure described below for opal glasses containing fluorine can be employed.

When the fluorine is present only as a minor constituent (say, when less than 1 per cent. is present) the silica determination can be carried out in the normal way (p. 228) without much loss of accuracy, and the bases can be determined in a sample decomposed with hydrofluoric and sulphuric acids. This procedure can be adopted, and the analysis much simplified, when a fluorine determination is not necessary, but when fluorine has to be determined the more complicated and tedious procedure (see below) must be used.

Lenses made of fluorspar have occasionally been introduced into optical systems and, if desired, the analysis of the raw material for such can be carried out as described for fluorspar on p. 154.

B. Opal and Alabaster Glasses

The analysis of white opal or opalescent glasses is dealt with in this section. The procedure for coloured opal glasses is the same, in general, except that it is sometimes advisable to determine the amount of colouring agent (by the methods described on pp. 272 to 281) in a separate sample.

The procedure to be adopted for the analysis of an opal glass depends upon the type of opacifying agent used (see p. 153). Modifications of the usual methods employed in silicate analysis are necessary for the complete analysis of most semi-opaque glasses, and suitable modifications for different types of such glasses are described below.

Minor constituents in these glasses are determined by methods to which reference is given below for each particular type of glass, and it should be noted that sulphates and chlorides are often essential constituents of alabaster and opal glass.

1. Glasses containing Fluorine: Phosphoric Oxide absent

With glasses containing more than 0·25 per cent. of fluorine, silica cannot accurately be determined in the usual way because part would be volatilised as silicon tetrafluoride during the evaporations to dryness (see p. 229). *Silica* and *fluorine* are therefore usually determined on the same sample by the following modified procedure:—One g. of the finely ground sample is fused with 5 g. of sodium carbonate at as low a temperature as possible. In the case of glasses or glazes very rich in fluorine and low in silica, 0·5 g. of sample is used and 1·0 to 1·5 g. of pure ignited silica, accurately weighed, is added to ensure complete decomposition upon fusion with sodium carbonate (see p. 228). The melt is extracted thoroughly with hot water, filtered and washed

(with hot water), the precipitate being reserved for the determination of silica and bases. The filtrate, which contains the fluorine and most of the silica as sodium salts, is nearly neutralised with dilute nitric acid (taking care that the solution never actually becomes acid) and treated with 4 to 5 g. solid ammonium carbonate. The mixture is then digested for some hours at about 40°, and allowed to stand overnight to precipitate silica and alumina. The bulky precipitate is filtered off, washed well with dilute ammonium carbonate solution and reserved.

The filtrate from the above precipitate still contains a small amount of silica, and therefore the filtrate and washings are together evaporated almost to dryness on a water-bath to remove the excess of ammonium carbonate. This evaporation is preferably carried out in a platinum basin, but porcelain may be used if platinum is not available. As considerable frothing, due to decomposition of ammonium carbonate, occurs during the evaporation, the basin must be covered by a clock-glass until the evolution of carbon dioxide is complete. The resulting mass is taken up with water, and the somewhat diluted solution neutralised carefully with nitric acid as recommended by Treadwell. The solution is coloured pink by means of a few drops of phenol-phthalein indicator, and the colour just discharged by the addition of 2 *N* nitric acid from a burette. The colour reappears on boiling, and, after cooling, is again discharged with nitric acid, the process being repeated until the addition of 1·0 to 1·5 c.c. of 2 *N* acid is sufficient to render the solution colourless. The solution is then treated with about 2 c.c. of Berzelius solution,[1] or preferably Seeman's solution,[2] the liquid boiled until the ammonia is completely expelled, and the precipitate, which contains the last traces of silica, is filtered off, washed with water and reserved.

Fluorine.—The filtrate from the above precipitate contains the fluorine, which is then determined as follows:—Dilute nitric acid is added to the solution until the sodium carbonate is nearly, but not completely, neutralised, as the solution must be slightly, but distinctly, alkaline. The solution is heated, a large excess of calcium chloride solution added, and the whole then boiled and filtered. The precipitate formed consists of calcium carbonate and fluoride, the presence of the former assisting in the filtration of the calcium fluoride, which is very slimy and difficult to filter if alone. If the glass under examination contains boric oxide, the precipitate also contains calcium borate.

The precipitate is washed on the filter paper with hot water, dried,

[1] *Berzelius solution* prepared by precipitating pure zinc chloride solution with potassium hydroxide, filtering, washing and dissolving the precipitate in ammonia.

[2] *Seeman's solution* prepared by dissolving to saturation moist freshly precipitated mercuric oxide in Schaffgotsch's solution (see p. 27).

separated as completely as possible from the filter, transferred to a platinum crucible and *gently* ignited. The filter is ignited separately and the ash added to the main portion of the precipitate. (Calcium fluoride precipitates should not be ignited in contact with filter paper.) Dilute acetic acid is then added to the precipitate in small quantities at a time, and in amount slightly in excess of that needed to dissolve the calcium carbonate (and borate, if present). When effervescence ceases the liquid is evaporated to dryness on the water-bath, the residue taken up with hot water and a drop of acetic acid, and the calcium fluoride filtered off, washed thoroughly and dried. The dried precipitate is transferred to a weighed platinum crucible as completely as possible, the filter paper burned separately and the ash added to the contents of the crucible, which is then gently ignited and weighed after cooling in a desiccator. With large calcium fluoride precipitates it is advisable to repeat the digestion with acetic acid and water, followed by filtration and gentle ignition as above to ensure the complete removal of calcium carbonate (and borate).[1]

The above method for fluorine (due to Berzelius[2]) requires careful attention to detail if accurate results are to be obtained. For very accurate work, to ensure that no fluorine is lost through retention by precipitates removed during the course of the analysis, it is advisable to ignite together the residue left after leaching the sodium carbonate fusion and the two silica precipitates, re-fuse the mixture with sodium carbonate and repeat the analytical process, adding the weight of calcium fluoride found to the weight of the first and major portion.

If the glass under examination contains sulphur trioxide, the calcium fluoride must be well washed to ensure absence of calcium sulphate, and in all cases it is advisable to check the purity of the weighed calcium fluoride by converting it to calcium sulphate.[3] (1 g. CaF_2 yields 1·7436 g. $CaSO_4$.)

When reporting analytical results, it is customary to state the percentage of fluorine in a glass rather than the percentage of a particular fluoride. When this course is followed in a complete analysis, the total of the individual percentages found exceeds 100 per cent., and, therefore, from such total is subtracted a percentage of oxygen equivalent to the percentage of fluorine present in order to obtain the correct total of the constituents determined.

[1] A slight loss of calcium fluoride occurs due to its solubility. According to Treadwell (Treadwell and Hall, *Analytical Chemistry*, 1919, vol. ii., p. 471), 100 c.c. water dissolve 0·0016 g. and 100 c.c. 1·5 *N* acetic acid 0·011 g. CaF_2 at the temperature of the water-bath.

[2] For a simplified and revised procedure for the Berzelius method, see Hoffman and Lundell, *Bur. Stand. J. Res.*, 1929, **3**, 581.

[3] Traces of fluorine in glass are best determined colorimetrically. See Hillebrand, *Bulletin* 700, *U.S. Geol. Survey*, 1919, p. 227, and Mellor, *A Treatise on Quantitative Inorganic Analysis*, 1913, p. 644.

Silica and Basic Oxides (other than alkali oxides) present in the sample are determined in the three precipitates removed prior to the precipitation of calcium fluoride (see above). As the precipitate obtained by the ammoniacal zinc oxide or mercuric oxide treatment contains matter not present in the glass sample, that precipitate is dissolved separately in hydrochloric acid, the solution evaporated to dryness, and the silica separated from the residue by dissolving the soluble portion in dilute hydrochloric acid and filtering. The silica precipitate is well washed, ignited, weighed and the weight noted; the filtrate from the silica is rejected. (Alternatively, if Seeman's solution has been used and the resulting mercuric oxide-silica precipitate well washed, the silica may be obtained ready for weighing by direct ignition, under a good draught hood, during which the mercury passes off.) The residue left from the original aqueous extraction of the melt, together with the precipitate obtained by ammonium carbonate (after drying and removal from the filter paper, which is incinerated and gently ignited, the ash being added to the precipitate), is then dissolved in hydrochloric acid, the silica separated in the usual way by evaporation to dryness (see p. 229), the weight determined and added to that previously found. The basic oxides other than alkali oxides are determined in the filtrate from the silica by the usual methods, the particular procedure to be adopted depending upon the actual bases present (see pp. 261, 256, 245 and 230).

Alternatively, the basic oxides can be conveniently determined on a sample decomposed by hydrofluoric and sulphuric acids (see p. 225).

Alternative Procedure for Silica.—According to Travers[1] silica can be quickly determined in silicates containing fluorine as follows. A ground sample is fused with potassium hydroxide in a silver crucible, extracted with water, boiled, cooled and filtered, the volume of the solution being kept as small as possible. (*a*) If alumina is absent or negligible, the precipitate is rejected, the filtrate treated in a silver dish with 1 g. of potassium fluoride for every 0·15 g. of silica present, hydrochloric acid is added to give an excess of 2 c.c. of concentrated acid, and finally 7 to 10 g. of solid potassium chloride is added for every 50 c.c. of solution. Under these conditions, the silica is precipitated quantitatively as potassium silicofluoride, which is filtered through a hardened filter in an ebonite funnel, washed with a 20 per cent. solution of potassium chloride until free from acid, then suspended in boiling water and titrated with $N/5$ potassium hydroxide to determine the silica.[2] An accurate blank determination should be made. Good results are claimed for this method. (*b*) If alumina is present in appreciable amount (as judged by the precipitate), the filter is punctured and the precipitate washed into the filtrate. The procedure

[1] *Comptes rend.*, 1921, 173, 714. [2] See p. 157 and Hilemann, *Z. anorg. Chem.*, 1906, 51, 159.

is then as above, except that nitric acid and potassium nitrate are employed instead of hydrochloric acid and potassium chloride, in order to avoid precipitation, as chloride, of silver from the crucible in which the fusion is made.

Alkali Oxides are determined by the Lawrence Smith method (see p. 235), potassium oxide, if present, being determined by the perchlorate method.

Boric Oxide, if present, can be determined by the usual methods, but if the fluorine content of the glass is appreciable, it is advisable to use acetic instead of hydrochloric acid for decomposing the melt (see pp. 249 and 252).

Minor Constituents.—Sulphur trioxide and chlorine are frequently essential minor constituents of opal and (particularly) alabaster glasses, and when present they can be determined as described on pp. 239 and 240. Other minor constituents can be determined in the usual way (see pp. 259, 236 *et seq.*).

2. Glasses containing Phosphoric Oxide: Fluorine absent

With such glasses, the usual analytical procedure has to be modified to (1) embrace a determination of phosphoric oxide and (2) effect a separation of the phosphoric oxide from the bases which have to be determined. A satisfactory modified procedure is as follows:—

One g. of sample is fused with 5 g. of sodium carbonate and the silica separated in the usual manner (see p. 228), but using *nitric* instead of hydrochloric acid. The silica so obtained is usually contaminated with more or less phosphoric oxide, and therefore it is treated to a final washing with warm dilute ammonia solution, the washings being collected separately, evaporated to dryness, the residue taken up with dilute nitric acid, and any silica present filtered off, the filtrate being added to that from the "second silica" precipitate.

The silica precipitates are ignited together in the usual manner and heated to constant weight. After weighing, the silica is treated with hydrofluoric and *nitric* acids, evaporated to dryness, ignited and re-weighed, the loss in weight indicating the weight of pure silica. As the residue after this treatment may contain phosphoric oxide, it is fused with a small amount of sodium carbonate, dissolved in hot dilute nitric acid and added to the main filtrate from the silica. (If antimony or tin is present, the silica will also be contaminated by antimonic or metastannic acid.) The combined solution of the constituents of the glass other than silica may be used for determinations as follows:—

If one or more of arsenic, antimony, tin and lead be present, the solution is placed in a conical flask, neutralised with ammonia, 2 to 2·5 c.c. of strong nitric acid added for each 100 c.c. of solution

and then heated to boiling. Hydrogen sulphide is passed into the gently boiling solution for about four hours, after which the flask is corked and set aside until the precipitate has settled completely. (It is advisable to allow the precipitate to settle overnight.) The precipitate is filtered off and washed, the filtrate and washings returned to the conical flask, heated to boiling and again treated as before with hydrogen sulphide for about three hours, after which any small precipitate formed is filtered off and washed.

If lead is present, the sulphide precipitates are dissolved in strong nitric acid and 2 to 3 c.c. of strong sulphuric acid in a covered beaker, the solution evaporated until dense white fumes of sulphuric acid are evolved, cooled, diluted when quite cold and the lead sulphate filtered off for the determination of lead as described on p. 257. Arsenic, antimony and tin may be determined in the filtrate from the lead sulphate (or directly from the sulphide precipitate if lead is absent), but they are best determined on separate samples as described on pp. 236 and 271. If the sample contains zinc, some zinc sulphide may be precipitated with the other sulphides, and it should be separated and determined as described on p. 248.

The filtrate from the sulphide precipitate is boiled until free from hydrogen sulphide, and barium, if present, should be removed at this stage by precipitation as sulphate with the least possible amount of dilute sulphuric acid (see p. 260).

Phosphoric Oxide. In the absence of barium, and it is not a frequent constituent of opal glass, the solution, freed from hydrogen sulphide, may be used for the determination of the phosphoric oxide or for the determination of the bases other than alkalis, and in many cases for both purposes. Alternatively, if barium is present, the filtrate from the barium sulphate is used for such purposes. In order to determine the bases other than alkalis, it is first necessary to remove the phosphoric oxide, and this is best done by precipitation as ammonium phosphomolybdate.[1] Thirty c.c. of ammonium nitrate solution (340 g. per litre) and 10 to 20 c.c. of nitric acid (sp. gr. 1·153) are added and the solution heated to boiling. The ammonium molybdate solution contains 30 g. per litre, and 1 c.c. will precipitate 0·001 g. P_2O_5. The necessary amount of this solution is heated to boiling and added to the hot phosphate solution either by means of a dropping funnel or by pouring slowly down a glass rod, stirring being maintained continuously. The hot liquid is stirred vigorously for a few minutes and then maintained at a temperature of about 50° for two to three hours to allow the precipitate to separate completely and settle out, after which the clear liquid is decanted through a filter paper, the precipitate washed by decantation with dilute acidified

[1] See Cauwood, Davidson and Dimbleby, *J. Soc. Glass Tech.*, 1929, **13**, 270.

ammonium nitrate solution (50 g. of ammonium nitrate and 40 c.c. strong nitric acid per litre) and filtered. The adhering precipitate need not be removed completely from the sides of the beaker at this stage. The filtrate and washings are saved.

If the amount of phosphoric oxide in the sample under investigation exceeds 0·1 g., the phosphomolybdate precipitate should be reprecipitated (as below) and then rejected, but if the phosphoric oxide present is less than 0·1 g., the precipitate can be used for its determination as follows: The phosphomolybdate precipitate is dissolved from the filter in warm dilute ammonia (1 : 40), the solution collected in the beaker in which the precipitate was formed, and the phosphoric oxide reprecipitated by adding 30 c.c. water, 20 c.c. of ammonium nitrate solution, and 1 c.c. of ammonium molybdate solution (strengths as before), heating to boiling and then adding 20 c.c. of hot nitric acid (sp. gr. 1·153), drop by drop with constant stirring, as a result of which the phosphomolybdate is reprecipitated in a pure condition. After standing for at least thirty minutes, the precipitate is filtered off and washed with dilute acidified ammonium nitrate solution as before, the filtrate being added to the filtrate from the first phosphomolybdate precipitate and the washings being rejected. The phosphomolybdate precipitate is again redissolved in warm dilute ammonia solution (1 : 40) and the solution nearly neutralised with hydrochloric acid until the precipitate which forms only just redissolves on vigorous stirring. An excess of "acid magnesia mixture" solution (consisting of 55 g. magnesium chloride and 105 g. ammonium chloride dissolved in 1 litre of water and made slightly acid with hydrochloric acid) is then added, the solution heated to boiling, a few drops of phenolphthalein added and dilute ammonia run in until a faint pink tinge just persists. The liquid is cooled somewhat and then one-fifth of its bulk of strong ammonia solution added with constant stirring. After standing three to four hours the crystalline precipitate is filtered off, dissolved in hot dilute nitric acid and reprecipitated as described on p. 234. The final magnesium ammonium phosphate precipitate is transferred completely to a filter paper, washed with cold dilute ammonia solution and then dried. After drying, the precipitate is detached as completely as possible from the filter, transferred to a weighed porcelain crucible, the filter paper being burnt separately and the ash added to the contents of the crucible, which is then ignited to constant weight, preferably in an electric muffle. The ignited precipitate consists of magnesium pyrophosphate, which contains 63·8 per cent. of P_2O_5.

If the sample contains more than 0·1 g. P_2O_5, phosphorus should be determined in a separate sample, containing not more than 0·1 g. P_2O_5, after decomposition with hydrofluoric and nitric acids, as below.

Bases other than alkalis can be determined in the combined filtrates from the phosphomolybdate precipitates, but it is necessary first to remove the excess of molybdenum. Two methods are available:—

(*a*) The solution is concentrated by evaporation to 350-400 c.c., carefully neutralised with ammonia and then acidified with 5 c.c. of concentrated hydrochloric acid. Ten g. of ammonium chloride is added, the solution boiled and the molybdenum precipitated immediately as lead molybdate with a hot 4 per cent. solution of lead acetate. After boiling, the lead molybdate is filtered off and washed with hot water until free from lead. The excess lead in the filtrate is precipitated with hydrogen sulphide after adjusting the acidity of the solution to 3 c.c. of hydrochloric acid (sp. gr. 1·16) per 100 c.c. of solution to prevent the precipitation of zinc (if present) as sulphide. The precipitated lead sulphide is filtered off and washed with hydrogen sulphide water. The filtrate from the lead sulphide is boiled until free from hydrogen sulphide, oxidised with a few drops of strong nitric acid, and the resulting solution, now free from phosphorus, molybdenum and lead, is used for the determination of the oxides of the metals (other than alkalis) present in the sample, the usual methods of analysis (see p. 245) being employed.

(*b*) The combined filtrates are evaporated with about 5 c.c. of concentrated sulphuric acid to a syrupy mass to expel all the nitric acid. The mass is taken up with 10 c.c. concentrated hydrochloric acid and 250 c.c. water, and hydrogen sulphide passed into the solution for about six hours, preferably in a pressure flask. After standing, the black precipitate of molybdenum sulphide is filtered off and washed with hydrogen sulphide water. The filtrate is subjected to a further treatment with hydrogen sulphide for two to three hours, and the second slight precipitate filtered off and washed as before. The filtrate is boiled to expel hydrogen sulphide completely and it can then be used for the determination of the oxides of the metals (other than alkalis) present in the samples according to the usual methods (see p. 245). The removal of the excess molybdenum as sulphide, as in this method, is more tedious than the removal as lead molybdate described above.

An alternative procedure for the determination of the phosphorus and the bases other than alkalis is to decompose a finely-powdered sample with hydrofluoric and nitric acids as described on p. 226, and then proceed with the precipitation of the phosphorus by ammonium molybdate in the resulting nitric acid solution, followed by the removal of the excess molybdenum and subsequent determination of the bases other than alkalis, as above. The phosphoric oxide determination should be made on a sample containing not more than 0·1 g. P_2O_5.

Other Constituents. The usual methods are employed for the determination of alkali oxides (see p. 235), boric oxide (p. 249), and minor constituents (pp. 259, 236 *et seq.*) present in phosphate opal glass.

3. Glasses containing both Fluorine and Phosphoric Oxide

In glasses of this type, (*a*) phosphoric oxide and bases other than alkalis are determined in a sample decomposed with hydrofluoric and nitric acids by the methods employed for phosphate glasses free from fluorine (see above); (*b*) alkali oxides, boric oxide and minor constituents are determined as in glasses containing fluorine with phosphoric oxide absent (see p. 262), and (*c*) silica and fluorine are determined as in fluoride glasses free from phosphate (see p. 262) subject to the following additional steps in the procedure:—

With these glasses, the filtrate from the last traces of silica (precipitated with either zinc oxide or mercuric oxide, see p. 263) contains the fluorine and some of the phosphorus in the sample, as alkali fluoride and phosphate respectively, together with a slight amount of alkali carbonate and a quantity of sodium nitrate. An excess of silver nitrate is added to this solution to precipitate silver phosphate and carbonate, the presence of the latter serving to correct any acidity resulting from the reaction between the silver nitrate and the phosphate. After gently heating, the combined precipitate of silver phosphate and carbonate is filtered off and washed with hot water. The excess of silver nitrate in the filtrate is precipitated by the cautious addition of sodium chloride solution and the mixture boiled to coagulate the silver chloride precipitate, which is then filtered off, washed and rejected.

Fluorine is determined in the filtrate from the silver chloride. As the solution is neutral, about 1 c.c. of $2N$ sodium carbonate solution is added, and the solution then boiled with a large excess of calcium chloride, the subsequent procedure being as described for fluoride glasses (see p. 263).

Silica is determined in the precipitates removed prior to the precipitation of the phosphoric acid with silver nitrate, the determination being carried out as described under fluoride glasses on p. 265.

As some of the phosphoric acid is carried down in the precipitates formed by sodium and ammonium carbonates in the early stages of the analysis (see p. 263), it is more convenient to determine the bases other than alkalis in the sample decomposed with hydrofluoric and nitric acids for the phosphoric oxide determination rather than to determine them in the sample decomposed with sodium carbonate for the silica and fluorine determinations.

4. Milky and Alabaster Glasses

Milky glasses, possessing only a slight degree of opalescence, usually owe this to the presence of chlorides or sulphates in the glass. The determination of these presents no special difficulty, and is carried out as described on pp. 239, 240. Alabaster glasses are rather more opaque than milky glasses and may contain small quantities of fluorine or phosphoric oxide in addition to chlorine and sulphur trioxide. Their analysis is carried out as previously indicated.

5. Dense White Opaque Glasses

Dense white glasses, which are used chiefly for such purposes as the threading in wine glass stems, the white line at the back of thermometer and Schellbach burette tubing and similar cases in which the tenuity of the opal layer is such that ordinary phosphate or fluoride opals would not be sufficiently opaque, are usually made by the introduction of considerable quantities of tin oxide into a lead glass.

Tin Oxide. Such glasses may usually be analysed by fusing 1 g. of powdered sample with 5-6 g. sodium carbonate and a little potassium nitrate, and treating the melt in the usual manner (see p. 228) but decomposing the fused cake with nitric instead of hydrochloric acid, evaporating the mass to dryness twice with a few drops of concentrated nitric acid, taking up the residue with hot dilute nitric acid and filtering off silica and stannic oxide together. After ignition, the weighed precipitate is evaporated with hydrofluoric and nitric acids and the loss in weight gives the true amount of silica present. The residue of tin oxide is fused with sodium carbonate, and the melt dissolved in hydrochloric acid, avoiding an excess of acid. The solution of stannic chloride so obtained is reduced by means of pure metallic iron and the stannous chloride formed titrated with standard iron solution,[1] or the solution may be neutralised with ammonia, boiled with strong ammonium nitrate solution after diluting to about 200 c.c. and the resulting precipitate filtered off, washed with hot dilute ammonium nitrate solution, dried, ignited strongly and weighed as stannic oxide. Other constituents are determined in the usual manner (see pp. 256, 261).

A rapid and useful method for control work is to fuse 1 g. of the powdered sample with 5 g. sodium carbonate and 1 g. sulphur. The aqueous extract of the melt is acidified with hydrochloric acid, the precipitated tin sulphide filtered off, washed with ammonium nitrate solution, dried and transferred as completely as possible to a porcelain crucible. The filter paper is ignited separately and the ash added to the contents of the crucible which is then ignited, gently at first, and finally at the full heat of a Méker or Teclu burner. After cooling, a

[1] J. W. Mellor, *A Treatise on Quantitative Inorganic Analysis*, 1913, p. 312.

little powdered ammonium carbonate is added and the crucible and its contents re-heated to constant weight. The precipitate is then stannic oxide, SnO_2.

Some dense opal glasses contain appreciable quantities of antimony oxide and also zirconia, as a substitute for the more expensive tin oxide. These constituents, if present, may be determined as described on p. 253 and p. 255.

C. Coloured Glasses

The analysis of coloured glasses is similar to that of colourless or opaque glasses except that sometimes modifications or special processes may require to be adopted to determine the amount of the colouring agent. In the first place, it is necessary to ascertain the general nature and composition of the glass itself in order to formulate a scheme for complete analysis. The glass is very often similar in composition to the simple glasses used for containers generally, *i.e.*, it is an alkali-lime-silica glass containing a small amount of alumina, with the colouring material in addition. In many other cases, the glass is a potash-lead oxide-silica glass coloured by the addition of special constituents. Common green bottle glasses and wine bottle glasses usually contain rather a high percentage of alumina. Coloured opaque glasses are similar in composition to opal and alabaster glasses except for the added colouring material. It might be noted that boric oxide is a more frequently occurring constituent of coloured than of colourless glasses, since it often assists in the development of the colour.

Having ascertained the general composition of the coloured glass under investigation by means of a preliminary qualitative analysis (p. 219), the methods to be adopted for the quantitative analysis are similar to those already described for non-coloured glasses of the same type (that is, whether lead-free or lead glass, borate, fluoride or phosphate glass, etc.), modifications of procedure being made, where necessary, to permit the determination of the colouring agent. As indicated on pp. 159 to 165, most of the colouring agents are metallic oxides, and they are determined by the usual methods employed in inorganic analysis. The following notes and special cases will be found of assistance.

Gold and Silver. These metals are used in the production of certain ruby glasses, usually, but not always, in potash-lead oxide-silica glasses. Often gold alone is used. Silver is occasionally, but very rarely, found in yellow glasses. The two metals can conveniently be determined by an assay method, as follows:—

Ten g. of the finely-powdered glass is thoroughly mixed with 8 g. of red lead (free from silver or with the exact silver content known), 20 g. of sodium carbonate, 5 g. of borax and 1 g. of flour. This

mixture is placed in a small fireclay crucible, covered with a layer of common salt and then melted in a small furnace for 1 to 1½ hours, after which the crucible is allowed to cool, and, when cold, broken up. The button of lead resulting from the fusion is removed from the slag and carefully cleaned. When quite clean, the lead is oxidised by cupellation on a porous bone-ash cupel in a small muffle furnace at a temperature of about 900°, and the resulting small bead of gold, or gold and silver, weighed. If silver is present, the bead is alloyed with about four times its weight of pure silver and "parted" with nitric acid in the usual way. (For details see Vol. II., p. 141 *et seq.*) If no gold is present, the bead will be completely soluble in nitric acid. With a gold ruby glass, it is always advisable to test for uranium as well as for silver, and tin oxide, which is always present, should be determined as described on p. 271.

Copper may be present as metallic copper or cuprous oxide in "copper ruby" glasses, or as cupric oxide in blue or green glasses. Copper ruby glasses are usually lead-free glasses of comparatively simple composition and the determination of the copper presents no great difficulties. Blue and green glasses containing copper are frequently rather more complex, especially the green glasses, as the copper may be associated with chromic oxide or uranium oxide. In any case the copper is precipitated as sulphide by hydrogen sulphide in the filtrate from the silica (see p. 230), arsenic, antimony and tin removed, if present, by washing the precipitate thoroughly with warm sodium monosulphide solution, the remaining residue dissolved in hot nitric acid and lead, if present, removed from the solution as lead sulphate after evaporation with sulphuric acid, as described on p. 257, the copper then being determined in the filtrate from the lead sulphate by one of the usual methods (see Vol. II., pp. 169-188).

Alternatively, copper can be determined in a fairly large sample decomposed by hydrofluoric and sulphuric acids. The residue from the decomposition is taken up with dilute sulphuric acid, lead sulphate if present is filtered off and the solution is then treated with hydrogen sulphide to precipitate the copper. The sulphide precipitate is treated as above, except that in this method, lead, if present, has already been removed. It should be noted that tin oxide is often present in copper ruby glasses.

Selenium. The method used for the determination of selenium will be decided by the amount probably present in the glass. In a ruby or pink glass the amount of selenium may be fairly considerable —0·2 to 0·5 per cent.—but if the determination of selenium as decoloriser in a colourless glass is required, the amount present is only of the order of 0·001 per cent. and a special method is called for.

In ruby glasses, the selenium is precipitated by hydrogen sulphide

in acid solution in the ordinary course of the analysis, but the determination is carried out on a separate sample, as follows: 2 to 5 g. of the finely powdered sample is weighed out and decomposed with hydrofluoric and nitric acids as described for the qualitative test on p. 220, the evaporations being made at as low a temperature as possible, and not taken quite to dryness, to avoid loss of selenious acid. The final residue is taken up with a small volume of dilute nitric acid, the solution then just neutralised with ammonia, after which strong hydrochloric acid is added to the extent of 1 in 3 by volume of the total solution, the selenium being determined in the clear solution as described on p. 165. Cadmium sulphide and zinc oxide are usually present in selenium ruby glasses.

The determination of selenium when it is present in such small amounts as are found in glass decolorised with selenium is best carried out by the method evolved by Cousen.[1] Twenty g. of very finely powdered glass is carefully dissolved in 50 c.c. of hydrofluoric acid and 30 c.c. of water in a platinum basin, keeping the solution as cool as possible during the process to avoid loss of selenium by volatilisation. After solution is complete, the contents of the basin are allowed to stand for an hour or two to permit the selenium to coagulate, and then poured into 800 c.c. of boiling water, when all but the selenium passes into solution. (If it is suspected that some of the selenium is in solution as selenious acid, then to ensure complete precipitation of the selenium, the original hydrofluoric acid solution is mixed with an equal bulk of hot, concentrated hydrochloric acid, and saturated with sulphur dioxide before being poured into the boiling water.) While still hot, the diluted solution is filtered through a thick pad of filter paper pulp in a Gooch crucible attached to a filter pump. The selenium is dissolved from the filter paper pad by dropping the latter into a beaker containing 10 c.c. of water, 5 c.c. of concentrated hydrochloric acid and 3-4 c.c. of a very dilute chlorine water (about *N*/60). The solution is gently warmed, the pad disintegrated with a glass rod, and the selenium passes readily into solution. The paper pulp is filtered off, washed with hot water, and the filtrate and washings made up to a 50 c.c. volume. When the solution is quite cold, the amount of selenium is determined colorimetrically as follows:—

The test solution is transferred to 100 c.c. Nessler cylinder, 1 c.c. of a 5 per cent. gum arabic solution and 5 c.c. of a 0·5 per cent. phenylhydrazine hydrochloride solution are added, the whole stirred and allowed to stand for fifteen minutes to develop the maximum depth of tint (a clear yellow). Simultaneously a series of standard comparison solutions are prepared in similar Nessler cylinders, using a standard dilute solution of sodium selenite (0·1 g. per litre) for the purpose.

[1] *J. Soc. Glass Tech.*, 1923, 7, 303.

Amounts of standard selenite solution in successively increasing quantities of 0·5 c.c. are added to the Nessler cylinders, then to each cylinder is added sufficient water to make a bulk of 50 c.c., followed by 1 c.c. of the gum arabic solution and 5 c.c. of the phenylhydrazine hydrochloride solution. After stirring the contents, these cylinders are allowed to stand for fifteen minutes, and then a range of tints of known selenium content is obtained. The amount of selenium in the test solution is determined by passing the Nessler tube containing it along the series of prepared standards and deciding which prepared solution has an equivalent depth of tint. The method gives results which are probably somewhat low, but they are accurate to about 0·5 c.c. of standard selenite solution, which is equal to 0·000023 g. selenium.

Cadmium is present as cadmium sulphide in most selenium ruby glasses and in some yellow glasses. The cadmium is precipitated by hydrogen sulphide in the ordinary course of the analysis, but particular attention must be paid to the concentration of the acid in the solution in which the precipitation is effected, since glasses containing cadmium sulphide frequently contain zinc oxide as a major constituent, and if the solution is too acid some of the cadmium may escape precipitation, whereas if the solution is not acid enough some zinc may be precipitated with the cadmium sulphide. According to Treadwell[1] a suitable concentration is 5 c.c. of concentrated hydrochloric acid to 100 c.c. of liquid. The hydrogen sulphide precipitate is washed with warm dilute sodium monosulphide solution to remove the sulphides of arsenic, antimony and tin, if present, and the residual cadmium sulphide dissolved from the filter by means of hot hydrochloric acid (1 : 2). The resulting solution of cadmium chloride is concentrated by evaporation after the addition of dilute sulphuric acid and finally transferred to a weighed porcelain crucible, in which the evaporation is continued on a water bath as far as possible and finally the excess of sulphuric acid is driven off by heating in an air bath, the crucible being supported inside a larger one by means of an asbestos ring. When fumes of sulphuric acid cease to be evolved, the outer crucible may be gently heated with a flame to ensure complete expulsion of free sulphuric acid, after which the crucible containing the cadmium, as sulphate, is cooled in a desiccator and weighed.

Lead is rarely, if ever, present in glasses containing cadmium sulphide, but if it should be present, it would be precipitated as sulphate when the solution of cadmium chloride (and lead chloride) is evaporated with sulphuric acid and can be filtered off, and determined as described on p. 257, the filtrate being subsequently evaporated to dryness for the determination of the cadmium as sulphate, as above. Any lead sulphide undissolved by the hydrochloric acid should be

[1] Treadwell (Hall), *Analytical Chemistry*, 1919, Vol. II., p. 193.

dissolved by hot nitric acid, the solution evaporated to fuming with sulphuric acid and the lead sulphate, treated as above, added to that obtained from the hydrochloric acid solution of the sulphide precipitate to determine the total lead present.

Sulphur is present as colouring agent in many amber bottle glasses, either alone or in conjunction with carbon. In such glasses it is believed that the colouring is due partly to colloidal sulphur and partly to iron sulphide. The total sulphur in a glass can be determined by fusing a 1 g. sample with 5 g. sodium carbonate and, say, 0·5 g. potassium nitrate and then proceeding as described for sulphur trioxide, p. 239. No method is yet available for determining the amount of colloidal sulphur in a glass, but Heinrichs[1] has worked out a method for determining sulphur as sulphide, according to which method 1 g. of finely powdered glass is decomposed with 25 c.c. of dilute hydrochloric acid (1 : 1) and 5 c.c. of hydrofluoric acid (48 per cent.) in a round-bottomed 150-200 c.c. flask in a current of carbon dioxide. The hydrogen sulphide so liberated is passed up a vertical Liebig condenser into a flask containing 30 c.c. of *N*/100 iodine solution, in which the hydrogen sulphide is absorbed and determined by a subsequent titration of the remaining iodine with *N*/100 sodium thiosulphate. Heinrichs found 0·08 per cent. of cadmium sulphide in a dark yellow glass and 0·02 per cent. ferrous sulphide in a brown glass.

Carbon is used for colouring certain amber bottle glasses, sometimes being used in conjunction with sulphur and sometimes with manganese. No suitable method for the determination of free carbon in glass has yet been evolved.

Iron Oxide occurs, sometimes in conjunction with chromium or with manganese, to the extent of 1—3 per cent. in many dark green bottle glasses and, in conjunction with manganese, in certain amber glasses. It is also present, usually with manganese and cobalt, in black bottle glass and, with cupric oxide, in certain green glasses made from pale green cullet (scrap glass) in small pot furnaces.

Ferric oxide is precipitated during the ordinary course of the analysis either with ammonia (after a preliminary separation with sodium acetate if manganese is present; see p. 279), and it may be determined in that precipitate (after fusion with potassium bi- or pyro-sulphate), or in a separate sample decomposed with hydrofluoric and sulphuric acids, by one of the methods described on pp. 171 to 178. Mellor[2] states that chromium interferes with the permanganate titration of ferrous iron, and therefore if it is desired to use a volumetric method when chromium is present, the iron should be reduced to the ferrous state with sulphur dioxide or ammonium

[1] *Z. anorg. Chem.*, 1927, **166**, 299; *J. Soc. Glass Tech.*, 1928, **12**, Abstracts, p. 88.
[2] J. W. Mellor, *Quantitative Inorganic Analysis*, 1913, p. 468.

bisulphite and then titrated with standard potassium dichromate solution (see p. 176). For further reference to iron and chromium occurring together, see below.

Chromium is found in so-called "actinic" green glasses, in certain green bottle glasses (in conjunction with iron oxide; see above), also in certain decorative green glasses where the colour is obtained by the combination of a yellow tint due to potassium dichromate and a blue tint due to cobalt or copper, and (rarely) in black glasses containing also iron, manganese and cobalt.

During the ordinary fusion of the glass with sodium carbonate (p. 228), part of the chromium is converted into chromate but is reduced to chromium chloride during the subsequent evaporations with hydrochloric acid to separate the silica, particularly if alcohol is added during the evaporation. After treatment with hydrogen sulphide for the removal of arsenic, lead, copper, etc., the solution is oxidised with nitric acid and the chromium usually precipitated as hydroxide, together with iron and aluminium, by ammonia in presence of ammonium chloride (see p. 230) and, after re-precipitation, that precipitate may be used for the determination of aluminium, iron and chromium according to either of the following procedures.

(*a*) The washed precipitate is dissolved in dilute sulphuric acid and an excess of ammonium persulphate added, together with sufficient sulphuric acid to prevent the precipitation of basic ferric sulphate. The solution is boiled, the chromium present oxidised to chromic acid, and then aluminium and iron are precipitated with ammonia and filtered off. The precipitate is dissolved in dilute sulphuric acid and the operations are repeated to obtain a precipitate free from chromium. The final precipitate of hydroxides is ignited and weighed; the iron oxide is determined colorimetrically or volumetrically after fusing the precipitate with potassium bi- or pyro-sulphate, and the alumina is estimated by difference.

Chromium is determined volumetrically or gravimetrically in the combined filtrates from the two iron and aluminium precipitates, it being present as chromic acid in that solution.

(*b*) Alternatively, the precipitate containing the aluminium, iron and chromium is ignited and weighed, then transferred to a silver crucible, well mixed with fifteen to twenty times its weight of sodium peroxide and cautiously fused. The resulting melt is digested with about 150 c.c. of water and cautiously boiled to decompose the peroxide; the iron is precipitated as ferric hydroxide, while the chromium and aluminium pass into solution as chromate and aluminate respectively. The iron precipitate is filtered off, dissolved in dilute acid, reprecipitated with sodium peroxide and again filtered off. The final precipitate is dissolved in dilute sulphuric acid, and the iron determined either

colorimetrically or volumetrically. The filtrates from the iron precipitates are combined, and the chromium (present as chromate) is determined colorimetrically (by comparison with a standard alkaline solution of sodium chromate) or volumetrically after acidifying, while alumina is again usually determined by difference, but if desired it can be precipitated by ammonia from the acidified solution for direct determination.

Chromium can be determined colorimetrically in a separate sample by fusing 1 g. of finely ground sample with 5 g. of sodium carbonate and 0·5 g. of potassium nitrate. The resulting mass is thoroughly extracted with water, filtered and the filtrate (which contains the chromium as alkaline chromate) made up to a standard volume and used for the colorimetric determination. If manganese is present, sodium manganate must be destroyed by heating the solution with a few drops of alcohol before making up to a standard volume.

It should be noted that chromium is not completely precipitated by the basic acetate process. Therefore, if it is necessary to precipitate aluminium, iron and chromium from solutions containing zinc or manganese (and with glasses such cases are rare), precipitation should be made with barium carbonate in the cold[1] or with ammonia, *making two or three reprecipitations.*

Uranium Oxide is the usual colouring agent found in canary-yellow transparent glasses, either of the lead oxide-potash or the lime-soda type. Uranium yellow glasses are characterised by a greenish fluorescence, much more pronounced in lime-soda than in lead oxide-potash glasses. Uranium is frequently encountered in conjunction with copper oxide (or, less frequently, cobalt oxide) in special shades of green glasses, particularly "antique" green tints in heavy lead glasses.

The separation of uranium from the other metals is carried out by ammonia or barium carbonate in the same way as for chromium (see above). Uranium, however, according to Mellor[2] tends to precipitate with lead, arsenic, copper, etc., when those metals are precipitated with hydrogen sulphide, and that precipitate should be redissolved and reprecipitated twice to ensure complete elimination of uranium from it. The uranium is usually precipitated with ammonia from the oxidised, combined filtrates from the lead, arsenic, etc., precipitate, and is separated from the aluminium and iron (see p. 230), and determined as follows: The precipitate (after reprecipitation) is dissolved in hot dilute hydrochloric acid, the solution made up to a bulk of about 150 c.c., 7-10 g. of ammonium chloride dissolved in a

[1] See Mellor, *Quantitative Inorganic Analysis*, 1913, p. 470, and Treadwell (Hall), *Analytical Chemistry*, 1930, Vol. II., p. 151.

[2] Mellor, *Quantitative Inorganic Analysis*, 1913, p. 490.

small volume of hot water added, the solution then transferred to a 400 c.c. conical flask and there treated with an excess of ammonium carbonate and then with colourless ammonium sulphide. The flask is corked and stood aside for some time, after which the precipitate (containing aluminium hydroxide and ferrous sulphide) is filtered off and washed with dilute ammonium sulphide solution; the filtrate contains the uranium as $(NH_4)_4UO_2(CO_3)_3$. The precipitate is dissolved in dilute hydrochloric acid, the hydrogen sulphide gently boiled off, the iron oxidised with nitric acid, and iron and aluminium determined in the resulting solution in the usual way. Uranium is determined by evaporating the filtrate almost to dryness, then making the solution slightly acid with hydrochloric acid, diluting, boiling and precipitating ammonium uranate with ammonia; the precipitate is filtered off, washed with faintly ammoniacal 2 per cent. ammonium nitrate solution, and finally ignited and weighed as U_3O_8 (see p. 164).

Manganese is present in various green, amber, and black bottle glasses, and in certain purple and violet potash-lead oxide-silica glasses. Its separation and determination during the ordinary analytical operations is described on p. 232, and its determination in a separate sample on p. 238. When iron and manganese occur together in a coloured glass, the iron should be precipitated by the basic acetate process during the analytical procedure for the determination of the bases (see p. 246).

If manganese and cobalt (or nickel, or both) occur together, as in certain black glasses, they are precipitated together as sulphides from an ammoniacal solution as described on p. 232, after any zinc present in the sample (and its occurrence in these glasses is rare) has first been removed by precipitation with hydrogen sulphide in the presence of formic acid (3 to 4 c.c. of formic acid, sp. gr. 1·2, per 100 c.c. solution). During the filtration of mixed manganese and cobalt (or nickel, or both) sulphides, the first portion of the filtrate is usually free from manganese, cobalt, etc., but the later portions, and especially the washings, almost always contain some of these metals, particularly if the filter is not kept full during the filtration process. The filtrate and washings should be tested by adding ammonium sulphide solution, then acidifying with acetic acid and boiling. Any precipitate which forms should be filtered off and treated later with the main sulphide precipitate. The mixed manganese, cobalt, etc., sulphide precipitates are dissolved in aqua regia, the solution boiled to expel excess acid, then neutralised with sodium carbonate and afterwards made slightly acid with acetic acid and diluted to 200 c.c. Sodium acetate (2 to 3 g.) is added to prevent the subsequent accumulation of hydrochloric acid, the solution heated to 70° to 80° and hydrogen sulphide passed in to precipitate the cobalt (or nickel, or both), the manganese remaining in

solution. The precipitate is removed by filtration through a close filter paper, and washed with dilute hydrochloric acid (sp. gr. 1·025) saturated with hydrogen sulphide to remove any manganese sulphide which may have been precipitated. The filtrate and washings are tested to ensure that the precipitation of cobalt (or nickel, or both) is complete, by evaporating to 50 c.c., adding an excess of colourless ammonium sulphide, then a slight excess of acetic acid, followed by warming; if cobalt or nickel is present, a small precipitate forms and it is filtered off and washed as before, the filtrate being again tested. The final filtrate (with washings) contains the manganese, which can then be determined in that solution (see p. 233). The combined precipitates contain the cobalt (or nickel, or both) and can be used for determination, as below.

Cobalt occurs as the colouring agent in blue glasses. It is also found in certain green glasses in conjunction with potassium dichromate (see p. 277) or uranium (see p. 278), and in certain black glasses with iron and manganese. As cobalt oxide is a very strong colouring agent, it only occurs in small percentages in glass. It is separated during the ordinary course of the analysis by precipitation as sulphide from ammoniacal solution as indicated under manganese (p. 279). If nickel is absent, the cobalt sulphide precipitate (obtained as above) is dissolved in aqua regia (after incineration of the filter paper), a few drops of sulphuric acid added, the solution evaporated to a small bulk, transferred to a weighed porcelain crucible and then evaporated completely to dryness, the cobalt being finally weighed as cobalt sulphate after ignition at 500°, the procedure being similar to that employed for the determination of cadmium as sulphate (see p. 275). If nickel is present, the precipitate of mixed cobalt and nickel sulphides is dissolved in aqua regia, chlorine boiled off, the solution diluted to about 100 c.c., 2 g. of ammonium chloride added, the solution made faintly ammoniacal, and the nickel precipitated as nickel dimethylglyoxime (see below) filtered off and weighed, cobalt being determined in the filtrate. Alternatively, the cobalt and nickel can be weighed together as oxides (after precipitation together with a minimum amount of potassium hydroxide), the nickel then determined by the dimethylglyoxime method in the solution of the mixed (weighed) oxides and the cobalt estimated by difference.

Nickel is present as colouring agent in certain violet glasses of the potash-lead oxide-silica type. During the ordinary course of an analysis, it is separated as sulphide from ammoniacal solution (see under manganese, above) and it is determined, after solution of the nickel sulphide in aqua regia, by precipitation with dimethylglyoxime in a faintly ammoniacal solution (see above, under cobalt) according to the standard procedure for that method (see Vol. II., p. 66).

Nickel can be determined in a separate sample decomposed with hydrofluoric and nitric acids (as described on p. 226). The resulting residue is dissolved in dilute nitric acid, filtered if necessary, the solution nearly neutralised with ammonia, 0·5 g. of ammonium acetate and 0·5 g. of tartaric acid added, the solution heated nearly to boiling, and then a slight excess of an alcoholic 1 per cent. solution of dimethylglyoxime is added to precipitate the nickel for weighing and determination, without having first to remove any of the other constituents of the glass present in the clear nitric acid solution.

D. Glass Enamels

Opaque and transparent enamels are used to a considerable extent in the decoration of glassware and also for printing inscriptions upon such articles as milk bottles, etc. In themselves the enamels are coloured glasses and can be analysed by the methods described on pp. 272 to 281. It may be noted, however, that the range of colours in glass enamels is greater than in the glasses themselves, as the temperature of maturing and time of firing is very restricted, so that colours can be produced in enamels that would be impossible in glasses under ordinary working conditions. As examples, coral-red enamels made from iron oxide or basic chromate of lead may be cited, also a range of scarlet colours produced by calcining various proportions of cadmium sulphide and selenium (or selenium dioxide) at a low temperature until a brilliant scarlet colour is fully developed, and then incorporating this colouring base with a very fusible flux by grinding the two together.

As the enamels must fuse and present a glossy surface at a temperature sufficiently low to avoid any risk of deformation of the glass articles to which they are applied (below 500° in the case of full crystal glasses), it is obvious that the flux must be very fusible indeed. This flux generally contains a high proportion of lead and boric oxides. This fact renders the analysis of enamel colours rather simpler than that of glasses similarly coloured, in that the finely-powdered enamels are usually completely decomposed by evaporation with nitric acid, so that the usual fusion with sodium carbonate is often unnecessary. Opaque enamels frequently contain tin oxide, which remains almost wholly with the silica when the sample is digested with dilute nitric acid and the mixture evaporated to dryness on the water bath, taken up with water and hot dilute nitric acid and the insoluble residue of silica and tin oxide filtered off. These may be ignited and weighed together, the silica driven off by evaporation with hydrofluoric and nitric acids (see p. 271) and the residual tin oxide ignited and weighed, the loss in weight representing silica.

The examination for boric oxide in these soft enamels is also simplified since the fusion with sodium carbonate may be omitted and the finely-ground sample directly decomposed by digesting with hydrochloric acid in a round-bottomed flask connected to a reflux condenser and proceeding as described on p. 249.

The separation and determination of the colouring materials is carried out as for coloured glasses (see pp. 272-281).

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A large amount of valuable information on the subject of glass analysis and the testing of the durability of glasses is only to be found in papers published in technical journals, particularly in the following :—

The Journal of the Society of Glass Technology.
The Journal of the American Ceramic Society.
The Bureau of Standards Journal of Research.
Glass Industry.
Glastechnische Berichte.
Sprechsaal.
Keramische Rundschau.

Amongst recent papers which give precision details for, or alternatives to, the methods described in the foregoing text are :—

"Note on the Determination of Boric Oxide in Glass," by Violet Dimbleby, *J. Soc. Glass Tech.*, 1930, **14**, 51.

"The Determination of Fluorine and of Silica in Glasses and Enamels containing Fluorine," by Hoffman and Lundell, *Bureau of Standard J. Research*, 1929, **3**, 581.

"'Taylor' Studies in the Technique of Analysis of Glass Raw Materials, III. Sodium Sulphate," by Dorothea Japhe, *Sprechsaal*, 1929, **62**, 8, 22.

"The Analysis of Soda-Lime Glass," by Lundell and Knowles, *J. Amer. Ceram. Soc.*, 1927, **10**, 829.

It should be noted that the Abstracts Section of the *Journal of the Society of Glass Technology* contains useful abstracts of all the papers on glass analysis and testing not published in that Journal itself, and in most cases those abstracts embody adequate working details.

CALCAREOUS CEMENTS

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I.—LIMESTONE AND PORTLAND CEMENT MIXTURES

LIMESTONE is the raw material used in the manufacture of quicklime, hydraulic lime and as an ingredient in the manufacture of Portland cement. Dolomitic limestone may be used in the manufacture of magnesium lime, but is said to be valueless as a raw material for Portland cement.

For analytical purposes the term limestone is here interpreted in its broadest sense to include all rocks composed largely or entirely of calcium carbonate. The upper limit is a limestone consisting entirely of calcium carbonate, but this degree of purity is rare; many of the commercially used limestones are very impure, and approach nearer and nearer to the point at which the term limestone is no longer applicable and the rock should rather be termed a calcareous clay, or shale. The authors have always regarded a rock containing approximately 50 per cent. of calcium carbonate as the lower limit for inclusion as a limestone. The transition between these extremes is gradual, and covers such materials as hard limestones, chalk, argillaceous limestones and marl. These materials are of different geological origin, and show a marked dissimilarity in physical properties, but the same method of chemical analysis may be applied to all, with slight modifications in the preliminary attack of the sample.

Sampling. When sampling quarries the greatest care must be exercised to ensure a true sample. This is particularly so when dealing with stratified formations such as occur in Lias deposits. Each stratum should be sampled separately, by breaking numerous pieces from its whole depth. As large a sample as possible should be taken since the average obtained by quartering a hundredweight, or even more, of material is more likely to be true, than a few pounds taken at random. When dealing with soft materials, such as chalk or marl, a sample of some depth from the face can be obtained by the use of an auger. Weathered pieces of rock should always be rejected, as the

process of weathering is invariably accompanied by a change in chemical composition. The sample from the quarry is broken down to pass a ½ in. mesh sieve. It is then thoroughly mixed, spread into a thin layer and divided into four quarters. Two alternate quarters are taken and broken to pass a ¼ in. mesh sieve. This portion is again mixed, and quartered. If a moisture determination on the original rock is required, the rejected portions at this stage can be further reduced, and the resultant sample utilised for this purpose. The other portion is roughly dried, broken down to a smaller size and the operation of quartering repeated. These operations are continued until about 30 g. of powder is available, and a few g. of this powder is further reduced to an extremely fine state in the agate mortar. For works purposes this portion is dried at 100° to 105°, and exact quantities weighed out for analysis. When the powder is extremely hygroscopic, or greater accuracy is required, the final drying is omitted, but a moisture determination must be made at the same time as the other portions are weighed out for analysis.

Preliminary and Works Tests. Before proceeding with the complete analysis of a limestone, it is necessary to know its approximate composition, in order that the correct method of attack may be applied. The tests described for this purpose are also utilised on the works for checking, rapidly and periodically, supplies of raw materials.

Gas - Volumetric determination of Calcium Carbonate. This is estimated indirectly, by decomposing a small quantity of the powdered limestone and measuring the volume of the evolved carbon dioxide. The extent to which magnesium carbonate if present is decomposed, and included in the estimation as calcium carbonate, depends largely on the type of apparatus employed. On decomposition with hydrochloric acid, magnesium carbonate evolves its carbon dioxide much more slowly than calcium carbonate; hence in apparatus of the Scheibler type, if the volume of gas is read off immediately after the initial evolution, the error is small, but where an apparatus of the Lunge and Rittener type is adapted, the whole of the magnesium carbonate is included in the estimation. Thus when using the Scheibler calcimeter, if, after the first evolution of carbon dioxide, a further increase in volume is noted, the presence of magnesium carbonate is indicated. This method of detecting the presence of magnesium is extremely approximate and is useful only to differentiate between negligible quantities of magnesium carbonate and amounts exceeding 2·5 to 3 per cent.

The following types of calcimeter are most suitable.

(*a*) The apparatus of Lunge and Rittener (p. 297), or Lunge and Marchlewski (Vol. I., p. 615), may be adapted. The total carbon dioxide is then estimated, and hence they are only suitable when the

limestone contains negligible amounts of magnesium carbonate. The carbon dioxide is calculated to calcium carbonate.

(*b*) The Scheibler Calcimeter, originally designed for determining calcium carbonate in animal charcoal used for sugar refining, is also

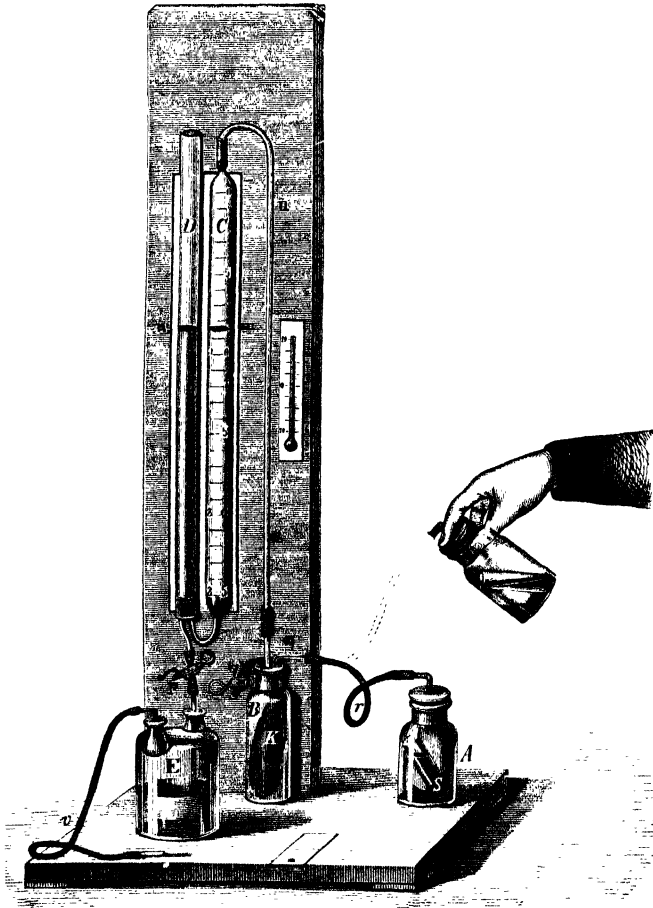



FIG. 44.

admirably suited for the examination of limestone and Portland cement mixtures.

The apparatus (Fig. 44) consists of a vessel (A) in which a weighed quantity of carbonate is decomposed, and containing a glass or gutta-percha tube of about 12 c.c. capacity, in which the acid required for the decomposition is placed. The vessel is closed by a perforated rubber cork, into which a short bent glass tube is fitted.

This is connected by means of rubber tubing with the centre vessel (B), from which the gas displaces air into the measuring apparatus. The vessel is closed by a cork with three perforations. Through one a bent tube passes connecting the first vessel; into another is fitted a long vertical tube connecting the centre vessel with the measuring apparatus; and into a third is fitted a short piece of glass tubing terminating in a piece of rubber tubing, closed by a spring or screw clip. This serves to connect the apparatus with the atmosphere at will. The measuring apparatus consists of two tubes firmly fastened to an upright board. These tubes are connected together below, and the left-hand tube is connected with a Woulff's bottle containing water used for adjusting the water levels in the measuring tubes. The right-hand tube has a capacity of 150 c.c., and is accurately graduated in half cubic centimetres. After fitting up the apparatus it should be proved to be airtight by adjusting the water level in the graduated tube at a much higher level than that of the other tube, and allowing the apparatus to stand for fifteen minutes, during which period no change of level should occur.

To carry out a determination, the barometer and thermometer are read, and the amount of substance to be weighed out then found by referring to the subjoined table (pp. 288-289); for instance, at 12° and 765 mm. pressure 0·4250 g. is weighed out. The powdered substance is introduced into the generating vessel, together with the small tube containing 5 c.c. of hydrochloric acid (sp. gr. 1·124). When all the corks and stoppers are fitted gas-tight, the bottle is tilted so that the acid flows over the material. The liberated carbon dioxide causes the bladder in the next bottle to expand, thus displacing air outside the bladder. This in its turn depresses the water in the large graduated tube, the water flowing into the other tube, which is not graduated, and thus causing the carbon dioxide to be under pressure. Before a reading of the volume of gas is taken, it is necessary to let water out of the plain tube until it is level with the water in the graduated tube. The carbon dioxide is then under atmospheric pressure. To the volume, when read off, a correction must be added for the carbon dioxide retained in the acid used for decomposition. Scheibler originally suggested 0·8 c.c. as the correction, but this estimate errs on the low side, and Warrington[1] later pointed out that the correction is not a constant quantity, but varies with the volume of gas evolved. He fixed 7 per cent. of this volume as the true correction. The total number of cubic centimetres of carbon dioxide equals the percentage of calcium carbonate in the material.

It has been suggested that corrections may be dispensed with by working in comparison with pure calcium carbonate; the relation

[1] *Chem. News*, 1875, 31, 253.

Table of the Weight of Substance to be Weighed out,

when 1 c.c. of carbon dioxide represents 1 per cent. of calcium carbonate, for barometric pressures of from 720 to 770 mm. and for temperatures from 10° to 25° C.

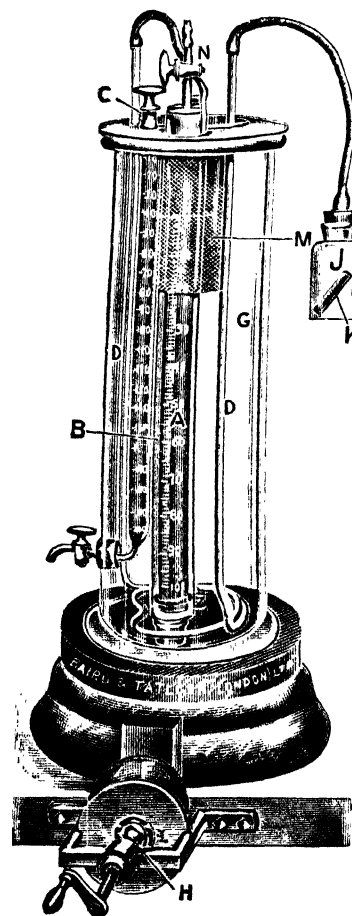
Temp. °C.	Millimetres.												
	720	722	724	726	728	730	732	734	736	738	740	742	744
10	0·4033	0·4044	0·4055	0·4067	0·4078	0·4090	0·4101	0·4112	0·4124	0·4135	0·4146	0·4158	0·4170
11	0·4015	0·4026	0·4038	0·4049	0·4060	0·4072	0·4083	0·4094	0·4106	0·4117	0·4128	0·4140	0·4151
12	0·3997	0·4008	0·4020	0·4031	0·4042	0·4054	0·4065	0·4076	0·4087	0·4099	0·4110	0·4121	0·4132
13	0·3979	0·3991	0·4002	0·4013	0·4024	0·4036	0·4047	0·4058	0·4069	0·4080	0·4092	0·4103	0·4114
14	0·3961	0·3973	0·3984	0·3995	0·4006	0·4017	0·4029	0·4040	0·4051	0·4062	0·4074	0·4085	0·4096
15	0·3943	0·3954	0·3965	0·3977	0·3988	0·3999	0·4010	0·4021	0·4032	0·4044	0·4055	0·4066	0·4077
16	0·3925	0·3936	0·3947	0·3958	0·3969	0·3980	0·3992	0·4002	0·4014	0·4025	0·4036	0·4047	0·4058
17	0·3906	0·3918	0·3929	0·3940	0·3951	0·3962	0·3973	0·3984	0·3995	0·4006	0·4017	0·4028	0·4039
18	0·3888	0·3899	0·3910	0·3921	0·3932	0·3943	0·3954	0·3965	0·3976	0·3987	0·3998	0·4009	0·4020
19	0·3869	0·3880	0·3891	0·3902	0·3913	0·3924	0·3935	0·3946	0·3957	0·3968	0·3979	0·3990	0·4001
20	0·3850	0·3861	0·3872	0·3883	0·3894	0·3905	0·3916	0·3927	0·3938	0·3949	0·3960	0·3971	0·3982
21	0·3831	0·3842	0·3853	0·3864	0·3875	0·3886	0·3897	0·3908	0·3919	0·3929	0·3940	0·3951	0·3962
22	0·3812	0·3823	0·3834	0·3844	0·3855	0·3866	0·3877	0·3888	0·3899	0·3910	0·3921	0·3932	0·3942
23	0·3792	0·3803	0·3814	0·3825	0·3836	0·3847	0·3857	0·3868	0·3879	0·3890	0·3901	0·3912	0·3922
24	0·3772	0·3783	0·3794	0·3805	0·3816	0·3826	0·3837	0·3848	0·3859	0·3870	0·3881	0·3891	0·3902
25	0·3752	0·3763	0·3774	0·3785	0·3796	0·3806	0·3817	0·3828	0·3839	0·3850	0·3860	0·3871	0·3882

Table of the Weight of Substance to be Weighed out—*continued*.

Temp. °C.	Millimetres.												
	746	748	750	752	754	756	758	760	762	764	766	768	770
10	0·4180	0·4192	0·4203	0·4214	0·4226	0·4237	0·4248	0·4260	0·4271	0·4282	0·4294	0·4305	0·4317
11	0·4162	0·4173	0·4185	0·4196	0·4207	0·4219	0·4230	0·4241	0·4253	0·4264	0·4275	0·4286	0·4298
12	0·4144	0·4155	0·4166	0·4177	0·4189	0·4200	0·4211	0·4222	0·4234	0·4245	0·4256	0·4267	0·4279
13	0·4125	0·4137	0·4148	0·4159	0·4170	0·4182	0·4193	0·4204	0·4215	0·4227	0·4238	0·4249	0·4260
14	0·4107	0·4118	0·4130	0·4141	0·4152	0·4163	0·4175	0·4186	0·4197	0·4208	0·4220	0·4231	0·4241
15	0·4088	0·4099	0·4110	0·4122	0·4133	0·4144	0·4155	0·4166	0·4177	0·4188	0·4200	0·4211	0·4222
16	0·4069	0·4081	0·4092	0·4103	0·4114	0·4125	0·4136	0·4147	0·4158	0·4169	0·4181	0·4192	0·4203
17	0·4050	0·4061	0·4072	0·4083	0·4095	0·4106	0·4117	0·4128	0·4139	0·4150	0·4161	0·4172	0·4183
18	0·4031	0·4042	0·4053	0·4064	0·4075	0·4086	0·4097	0·4108	0·4120	0·4131	0·4142	0·4153	0·4164
19	0·4012	0·4023	0·4034	0·4045	0·4056	0·4067	0·4078	0·4089	0·4100	0·4111	0·4122	0·4133	0·4144
20	0·3993	0·4004	0·4015	0·4025	0·4036	0·4047	0·4058	0·4069	0·4080	0·4091	0·4102	0·4113	0·4124
21	0·3973	0·3984	0·3995	0·4006	0·4017	0·4028	0·4039	0·4050	0·4061	0·4072	0·4082	0·4093	0·4104
22	0·3953	0·3964	0·3975	0·3986	0·3997	0·4008	0·4019	0·4030	0·4041	0·4052	0·4062	0·4073	0·4084
23	0·3933	0·3944	0·3955	0·3966	0·3977	0·3988	0·3998	0·4009	0·4020	0·4031	0·4042	0·4053	0·4064
24	0·3913	0·3924	0·3935	0·3945	0·3956	0·3967	0·3978	0·3989	0·3999	0·4010	0·4021	0·4032	0·4043
25	0·3893	0·3904	0·3914	0·3925	0·3936	0·3947	0·3958	0·3968	0·3979	0·3990	0·4001	0·4012	0·4022

between the amount of carbon dioxide evolved from a given weight of this substance and that evolved from an equal weight of the material under test being a simple proportion. For the regular testing of Portland cement mixture it is much better to work against a standard sample of normal material, of accurately known composition. Comparisons of this nature only hold good provided the temperature and barometric pressure remain unchanged while the two determinations are being carried out. Hence they should be made as speedily as possible.

Fig. 45.

(*c*) Clarke's Calcimeter. The principle is the same as the Scheibler apparatus, in that the gas liberated by the action of hydrochloric acid on the carbonate displaces a corresponding volume of water. The whole apparatus is enclosed in a water jacket to maintain an equable temperature throughout the operation. The apparatus is illustrated in Fig. 45. The bladder is dispensed with, the carbon dioxide having direct access to the body of the apparatus, through the cooling coil. The graduated tube is concentric with the plain one, and fine adjustment of the levelling carried out by means of a bellows fitted on the stand, and having a screw adjustment. The burette for holding the hydrochloric acid is also enclosed in the water jacket, so that the acid required is at the same temperature with the rest of the apparatus. The method of working the calcimeter is as follows:—The water jacket, tubes A and B, and the nearly closed bellows are fitted with water. Care must be exercised to ensure that no air is left in the bellows. The joints should be tested to see if they are gas-tight by closing the stopcock N and opening the bellows so that there is an appreciable difference of head between A and B. Any leak will be revealed and can be remedied. The water level is then restored.

A weighed portion of dried material is placed in the bottle J, and 10 c.c. of hydrochloric acid (sp. gr. 1·112) run into the tube K, which is carefully placed in the bottle. This is closed with its stopper, and

immersed in the cage in the water jacket. As soon as the temperature is constant, the water in the tubes A and B is adjusted to zero by means of the bellows and the stopcock N. The bottle J is then taken out and tilted so that the acid flows over the material. While the carbon dioxide is being liberated, the bellows F is slowly opened so that the water levels in A and B remain nearly the same. When the reaction is complete, the liquid in the bottle is swirled round for half a minute to expel the excess of carbon dioxide from the supersaturated liquid. The bottle is then placed in the cage in the water jacket for about two minutes, the levels in A and B once again adjusted to equal and the reading taken. The volume of the moist gas so obtained is calculated to its equivalent weight of calcium carbonate, corrections being made for the pressure, temperature, moisture and amount of gas in solution in the apparatus. Tables are supplied with the apparatus to furnish all necessary corrections.

(*d*) Faija Calcimeter. In principle this apparatus resembles that of Scheibler and Clarke, but it further incorporates a means of measuring the gas at 760 mm. pressure, so that only the temperature correction need be considered. The apparatus is illustrated in Fig. 46. It consists of a gas measuring tube E, having at its upper end the taps F and G, and connected via the lead cooling coil with the gas generating bottle A. The lower end of E is connected with the equilibrium tube H, which can be moved up and down, and secured in any position by fixing it in the rod I with the thumbscrew K. To the other end of H is connected the barometer L. N is an india-rubber ball attached also to the barometer. The ball may be compressed or allowed to expand by suitably turning the handle O, thus adjusting the pressure in the barometer. Before using the apparatus it should be proved airtight by closing F, placing the equilibrium tube H in such a position that the water level in E and H differs by several inches, and noting the reading in E. If airtight this reading will be constant over any prolonged period.

The levelling tube H is adjusted so that the level of the water in E coincides with the mark immediately under tap F, and fixed in position by the thumbscrew K. The carbonate is weighed out and transferred to the decomposition bottle A; 10 c.c. of hydrochloric acid is introduced into the gutta-percha container C, which is carefully placed in A. The stopper of A is then inserted and the tap G is closed. The thumbscrew K is then slackened with the left hand, at the same time maintaining H in approximately the same position. With the right hand the generating bottle A is tilted, so that the acid runs over the carbonate. As the gas is generated, the levelling tube H is lowered, so that the level of liquid in E and H remains about equal. When the gas is completely generated the bottle A is well shaken and placed in D for a few minutes. The taps F and M are

then closed and the handle O turned in the requisite direction until the barometer indicates 760 mm. The tube H is finally adjusted until the levels of liquid in E and H are coincident, the temperature noted and the reading of E taken. This reading is the volume of gas evolved

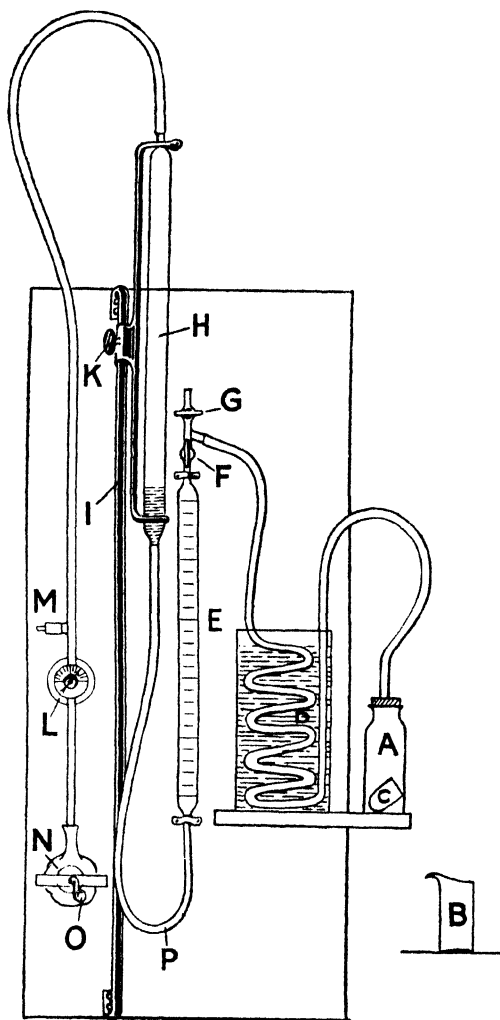



FIG. 46.

under the standard pressure of 760 mm., and simply requires correction for temperature. This is carried out by tables supplied with the instrument, thus enabling the operation of testing to be carried out in a few minutes. No correction for absorption is necessary as this is allowed for in the graduation of the measuring tube.

Alkalimetric Determination of Calcium Oxide or Carbonate. The calcium oxide or carbonate in a limestone can also be determined by titration. For this purpose 1·0 g. of the powdered substance is weighed into a flask, covered with a little water, and decomposed by the gradual addition of 25 c.c. of *N*/1 hydrochloric acid. The liquid is then boiled to drive off carbon dioxide, and after cooling, titrated back with normal sodium hydroxide, using phenolphthalein as an indicator. The number of cubic centimetres of normal acid required are simply multiplied by 5 or 2·8 to give the percentage of calcium carbonate or oxide respectively, in the substance.

Methyl orange may be used in place of phenolphthalein. While not so delicate, it is not necessary to boil off the carbon dioxide if this indicator is used.

When the limestone contains a notable amount of magnesia, the calcium and magnesium can be determined together by titration according to the method of Newbury,[1] with sufficient accuracy for technical purposes. The method is based on the facts that magnesium hydroxide is sufficiently soluble in water to colour phenolphthalein, and that, when boiled in dilute solution with sodium hydroxide, magnesia is completely precipitated and separated from calcium oxide. 0·5 g. of the limestone is weighed into a conical flask of about 500 c.c. capacity, fitted with a rubber stopper, and a thin walled glass tube about 75 cm. long, which serves as a reflux condenser. Sixty c.c. of *N*/5 hydrochloric acid is then added, the condenser inserted, and the liquid boiled gently for about two minutes, care being taken that no vapours escape. The tube is rinsed with a little water and removed, and the flask cooled under the tap; 5 to 6 drops of phenolphthalein solution (1 g. in 200 c.c. of alcohol) are then added and the solution titrated to a faint pink colour with *N*/5 sodium hydroxide. It is most important to hit the point at which a slight pink tinge suffuses the liquid, even if it be transitory, for if alkali is added until a decided permanent coloration is formed, the lime will come out too high. The volume of acid employed may be called "first acid," and that of the alkali required "first alkali." In limestones containing insignificant amounts of magnesia this completes the determination and No. of c.c. of acid – No. of c.c. of alkali × 2 × 0·56 = per cent. CaO.

Determination of Magnesium Oxide. To determine the magnesia the process is continued as follows. The neutralised solution is poured into a large test tube 30 cm. long and 2½ cm. bore, furnished with a mark at a volume of 100 c.c. To the boiling liquid *N*/5 sodium hydroxide is gradually added c.c. by c.c., the boiling being repeated after each addition, until a strong red coloration persists on continued boiling. With a little practice this point can easily be judged to half a

[1] *Cement and Eng. News*, 1903, 14, 35.

c.c. The alkali thus added to the neutralised liquid may be called "second alkali." The liquid is made up to 100 c.c., boiled for a moment, and allowed to stand until the precipitate has settled. 50 c.c. of the clear supernatant liquor is then withdrawn with a pipette and titrated back with $N/5$ acid until colourless. The volume of acid required is multiplied by 2 and called "second acid." The calculations are then as follows:—

Second alkali − second acid . . . $\times 2 \times 0.40$ = per cent. MgO
First acid − (first alkali + second alkali + second acid) $\times 2 \times 0.56$ = per cent. CaO

The excess of alkali used in precipitating the magnesia should not exceed 1 c.c., hence the "second acid" should not exceed 1 c.c., otherwise the magnesium hydroxide carries down some calcium hydroxide.

This method tends to give results too high for magnesia and too low for lime, partly due to the formation of calcium carbonate, owing to the action of atmospheric carbon dioxide during the separation of magnesia. By the use of a large test tube, as prescribed, this source of error is reduced to a minimum. Again, too little lime may be found when the calcium occurs in the limestone in the form of compounds such as felspar, which are not decomposed by dilute acids. All alkalimetric and calcimetric methods are subject to this defect, but notable quantities of insoluble lime occur very rarely in limestone. Much soluble alumina and ferric oxide, if present, somewhat obscure the end point in the first and second titrations. When alumina is precipitated by sodium hydroxide, however, the red coloration does not appear until all the alumina has come down, hence the proportion of magnesia is not increased by the soluble alumina present.

The method described above is thoroughly serviceable for fairly pure materials, but does not give such good results on calcareous marls. This is not exclusively due to a little lime in the form of silicates insoluble in dilute acids. In the second titration with sodium hydroxide the bulk of the precipitate, which consists largely of insoluble matter, makes the end reaction more difficult to recognise; the coloration must be unmistakably deep red. In limestones containing much silica, alumina, and ferric oxide, the volume of liquid will exceed 100 c.c. and it is therefore advisable to use a more capacious measuring vessel from the beginning.

Complete Analysis

In a complete analysis of a limestone the following determinations are usually required: Loss on ignition (this includes carbon dioxide, organic matter, combined water, etc.), silica, alumina, ferric oxide, calcium oxide, magnesium oxide, total sulphur, sulphur occurring as

sulphuric acid, carbon dioxide, and alkalis. A moisture determination on the original rock may be called for, and occasionally a separate examination of the clayey matter. For technical purposes the determination of other constituents, usually present in only minute quantities, is not required. They have no bearing on the commercial application of the limestone, and do not seriously affect the accuracy of the results obtained by the following methods. For the exhaustive analysis of rocks and minerals, the works of Washington,[1] or Hillebrand,[2] should be consulted (see also Clays, p. 19).

Moisture. If it is desired to determine the moisture on the original material, the sample from the quarry must be immediately enclosed in an air-tight container, and the determination made with the least possible delay. Some crushing is desirable, in order to expedite the removal of the moisture, but this should not be carried further than is absolutely necessary, as water is easily dissipated in this operation. A satisfactory determination may be made on soft materials which have been crushed to pass 10 I.M.M. screen, but for hard materials it is sometimes desirable to crush finer. 100 g. of the material is weighed out, and placed in a wide glass tube. This is heated for two hours at 105° during which time dry air is drawn over the material. The loss in weight gives moisture.

Method of Attack. Few limestones are so pure that they leave no residue on treatment with hydrochloric acid. They may contain quartz, clay or other silicates, carbonaceous matter, or pyrite. The mode of attack depends on the amount of insoluble matter. At this stage, the information available from a calcimetric examination of the material will suffice to indicate which of the following procedures should be adopted.

(*a*) By solution in acid after strong ignition. This is the best method to employ when the amount of insoluble matter does not exceed that which is present in a Portland cement mixture. Limestones in which this limit is not exceeded are converted into a product, wholly soluble in hydrochloric acid, by heating for twenty to thirty minutes at a temperature of 1100° to 1200°. A good blast flame is necessary for the attainment of this temperature, and in addition, the limestone must be in a finely powdered condition.

(*b*) By solution in acid after heating with sodium carbonate. When the amount of siliceous compounds exceeds that enumerated above, a wholly soluble product is not formed by strong ignition alone, and it is necessary to mix in a small quantity of sodium carbonate to assist in

[1] *Manual of the Chemical Analysis of Rocks*, Henry Washington, London: Chapman and Hall, 1904.

[2] "The Analysis of Silicate and Carbonate Rocks," W. F. Hillebrand, *Bulletin* 700, *United States Geological Survey*.

the decomposition. A liquid fusion is unnecessary, as the lime formed by the ignition is itself a powerful flux, and serves to decompose part of the silicates. 0·5 g. of sodium carbonate is ample for the purpose. By this means sodium compounds which might prove objectionable in subsequent separations are kept to a minimum.

Silica. 0·5 g. of the sample is weighed out and transferred to a platinum crucible, and treated as in (a) or (b), according to its composition. The subsequent procedure is as described on p. 339.

Oxides of Iron and Aluminium are determined as on p. 340. As a general rule it will be found that when the washings from the precipitate show a negative test for lime, they will also show a negative test for chlorides. As a further safeguard some workers prefer to dissolve the first precipitate in nitric acid, thus avoiding the presence of chlorides in the second precipitation. The precipitate is ignited and weighed as mixed oxides. For comparatively pure limestones, mixed oxides, reported as such, will suffice. Where a separation is required it should be conducted by one of the methods described on p. 4.

Calcium Oxide and *Magnesium Oxide* are determined as on p. 340.

Total Sulphur. One g. of the sample is mixed with 4 g. of sodium carbonate and 0·5 g. of potassium nitrate in a platinum crucible, and the mixture fused or the method described on p. 13 is used.

Sulphur as Sulphuric Anhydride. One g. of the sample is weighed into a small beaker, swirled round with a few c.c. of water, and 10 c.c of hydrochloric acid added. After boiling for a few minutes, the contents of the beaker are filtered and washed, and the filtrate diluted to about 200 c.c. The barium sulphate is precipitated as in the total sulphur estimation. Sulphur in the oxidised form is sometimes reported as sulphur trioxide, but more frequently as calcium sulphate. Barium sulphate contains 34·3 per cent. of sulphur trioxide. The sulphur existing in this form should be deducted from the total sulphur, to enable the sulphur present as sulphide to be computed. *Cf.* also p. 15.

Alkalis. One g. of sample is mixed with its own weight of pure resublimed ammonium chloride, and 6 g. of pure precipitated calcium carbonate and the determination carried out as on p. 9.

When the mixed chlorides have been weighed the potassium may be determined by the perchloric acid or the platinum chloride method (p. 10).

Loss on Ignition. One g. of the sample is weighed into a platinum crucible, and the weight of the crucible and contents noted. It is heated over the blast flame to constant weight. The loss in weight is reported as loss on ignition. For limestones which form an acid soluble product on ignition alone, this determination can be carried

out on the portion taken for silica, etc., and the crucible and contents weighed before the acid extraction is proceeded with. In other cases a separate portion must be taken.

Carbon Dioxide. An accurate determination of this constituent can be made by any of the methods detailed below. (*a*) Method of Fresenius (gravimetric) (see p. 12).

(*b*) Method of Lunge and Rittener. The carbonate is decomposed by hydrochloric acid, and the evolved carbon dioxide absorbed in a strong solution of caustic potash. By noting the temperature and

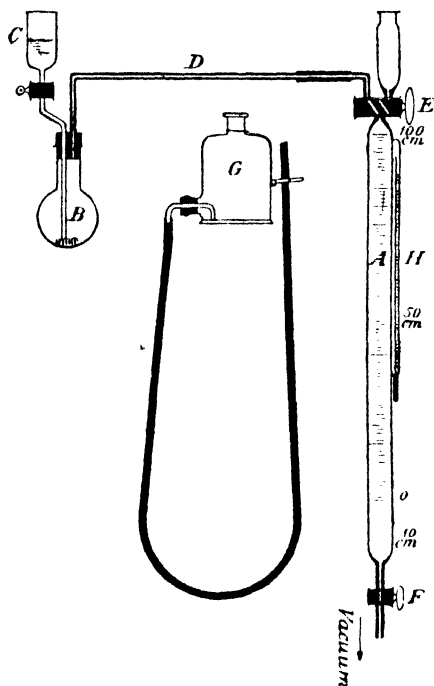



Fig. 47.

pressure, and measuring the volume of gas before and after absorption, the amount of carbon dioxide can be computed exactly. The apparatus is illustrated in Fig. 47.

Procedure. Into the decomposition flask B is placed about 0·15 g. of the calcite or a corresponding amount of any other carbonate. A small piece of aluminium wire weighing about 0·015 g. is fastened to the glass tube inside the flask at a point just below the cork. One c.c. of water is introduced through the funnel C and the capillary is connected to the dry Bunte burette. The stopcock of the funnel C is closed, the flask and bulk put into direct communication by suitably adjusting the stopcock E and the other end of the burette connected

to a suction pump, F being open. A partial vacuum is then produced in the burette by allowing the suction pump to run for two or three minutes, after which the F is closed. Hydrochloric acid 1 to 4 is then allowed to flow upon the substance, after which the liquid is heated to boiling, care being taken that no water enters the burette. More acid is then added to the contents of the flask until the aluminium wire is covered and the flask heated again. The hydrogen evolved serves to expel the last traces of carbon dioxide from the liquid. As soon as all the aluminium is dissolved, hydrochloric acid is added through the funnel C until the liquid reaches the stopcock E, which is then closed. The lower end of the burette is then connected by rubber tubing with the levelling tube from G, which contains a saturated solution of common salt. The stopcock F is opened and the salt solution allowed to rise in the burette. The levelling bottle is adjusted until the liquid in both vessels stands at the same level, whereupon F is closed. The apparatus is allowed to stand for twenty to twenty-five minutes, so that the temperature of the gas will be that of the surroundings, and then by again adjusting the levelling bottle with F open, the burette reading is taken, and the temperature and atmospheric pressure noted. The funnel of the burette is filled with strong caustic potash solution (1 : 2), and a partial vacuum is obtained in the burette by lowering the levelling tube, F being open. The caustic potash is allowed to enter the burette by opening E, which should be closed before the last drops of liquid leave the funnel. The contents of the burette are then shaken. The residual volume of gas is measured with the usual adjustment of levelling tube, and the difference between the two readings gives the volume of carbon dioxide absorbed. In making the final calculation it should be noted that the vapour tension of a saturated solution of salt is only 80 per cent. of that of pure water at a like temperature.

Example.

Weight of substance . .	a		
Temperature	t	Volume of air + hydrogen + CO_2	V
Barometric pressure . .	B	,, ,, ,,	V_1
Tension of aqueous vapour	w mm.	,, CO_2	$V - V_1$
,, ,, salt solution .	0.8 w		

Volume reduced to N.T.P. $= \frac{(V - V_1)\ (B - 0{\cdot}8w)\ 273}{760\ (273 + t)} = V_0$

Density of carbon dioxide (air as unity) = 1.529

1 c.c. of air at N.T.P. weighs 0.001293 g.

1 ,, CO_2 ,, ,, 0.001977 ,,

And per cent. CO_2 in sample $= \frac{V_0 \times 0.1977}{a}$

Determination of Clay. When the calcimetric or alkalimetric method shows that much clay is present in a limestone, a separate estimation of argillaceous matter is sometimes required. 5 g. of the powdered material is weighed into a porcelain dish, which is half filled with water, and hydrochloric acid added to slight excess. The contents of the dish are heated to expel carbon dioxide and then filtered through a tared filter paper. The residue is well washed and dried with filter at 105° to constant weight. The increase in weight represents the clay and quartz, etc., in the quantity taken. After weighing it is removed from the filter paper, finely powdered in an agate mortar, and preserved in a stoppered weighing tube. Its analysis should be conducted as described under clay (p. 2 *et seq.*), omitting the determination of sulphur as sulphate, which will be found in the hydrochloric acid solution.

Rapid Determination of Lime. A rapid and accurate estimation of lime only is sometimes required. This may be made by either of the following methods.

(*a*) About 0·25 g. of limestone or raw mixture is weighed out and transferred to a beaker. It is treated with 5 c.c. of hydrochloric acid and a few drops of nitric acid, evaporated to dryness and heated to drive off nitric fumes. The dried mass is treated with dilute hydrochloric acid, boiled and filtered, the residue being well washed with hot water. The filtrate is rendered slightly alkaline with ammonium hydroxide, brought to boiling, and dilute acetic acid added, until the hydroxides of iron and aluminium have redissolved. The lime is then precipitated by the addition of a hot solution of ammonium oxalate, and the boiling continued for two minutes. Calcium oxalate settles rapidly as a granular precipitate, but its complete separation should be ensured by cooling the beaker in cold water. The precipitate is collected on a filter paper and washed with warm water until free from ammonium oxalate. The filter paper is opened out and the adhering precipitate washed into a beaker, the paper being retained. Dilute sulphuric acid, 1 to 10, is poured over the precipitate and the resultant solution heated to 80° and titrated with standard potassium permanganate. The filter paper is introduced into the liquid, which is stirred for a few moments. The pink coloration will be destroyed, and the addition of the standard potassium permanganate is continued drop by drop, until a permanent coloration is re-obtained.

The addition of nitric acid in the preliminary attack of the sample is intended to destroy any organic matter which may be present. As an alternative procedure the sample may be ignited at a bright red heat for a few minutes and then dissolved up in hydrochloric acid alone. Even so, with Portland cement mixtures an evaporation to dryness is advisable, otherwise the precipitated calcium oxalate

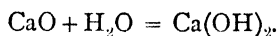
is liable to contain gelatinous silica which renders the filtration exceedingly slow. A convenient strength of potassium permanganate solution is 5·64 g. per litre. One c.c. of this solution is equivalent to 0·005 g. of CaO. The solution should be standardised against sodium oxalate.

(*b*) The following method is advocated by Richard K. Meade.[1] 0·3 g. of raw material or limestone is weighed off and strongly ignited over the blast flame for a few minutes to destroy organic matter. It is transferred to a beaker and boiled with dilute hydrochloric acid until decomposition is complete. Ammonium hydroxide is cautiously added until a slight permanent precipitate is formed and 10 c.c. of a 10 per cent. solution of oxalic acid is added. This method depends on the fact that oxides of iron and aluminium are soluble in oxalic acid, and that calcium oxalate is not. The mixture is stirred until these oxides are entirely dissolved. The solution is made up to about 200 c.c. boiled, and sufficient boiling saturated solution of ammonium oxalate is added to precipitate the lime, and the boiling continued for two minutes. The solution is cooled by immersing the beaker in cold water, filtered and the precipitate is treated as in the preceding method.

II.—LIMES AND HYDRATED LIME

Commercial limes are composed of calcium oxide together with varying amounts of magnesium oxide and argillaceous matter (clay). The presence of the latter is important, since it is frequently the cause of valuable hydraulic properties. Certain inert compounds (quartz, etc.) are nearly always found, but these may be regarded as impurities of no value and should not exceed 5 per cent. Limes are usually marketed under one of the following classes:—

Quicklime. Quicklime is obtained by calcining high calcium limestone at a white heat; it combines with water and carbon dioxide with great avidity. When a small quantity of water is poured upon quicklime the mass becomes hot, and volumes of steam are given off, the lime at the same time swelling up and crumbling to a soft dry powder. This process is known as the slaking of lime, and the product is termed slaked lime. The reaction which takes place is represented by the equation:—

$$CaO + H_2O = Ca(OH)_2.$$

Hydraulic Limes. Hydraulic limes differ from quicklime in that the slaking effect on adding water is extremely slow, but they subsequently set to a hard mass. The hardening process also takes

[1] *Portland Cement*, 1926, p. 456.

place under water, a quality not possessed by quicklime. They are obtained by the calcination of argillaceous limestone, at a temperature somewhat lower than that used in the manufacture of quicklime.

Magnesium Limes. These are formed by the calcination of dolomitic limestone. They slake very slowly and expand rather less than quicklime. The only reliable test which distinguishes them from a calcium lime is a chemical analysis. A magnesium lime will contain over 10 per cent. of magnesium oxide, but some Italian magnesium limes contain up to 40 per cent. of magnesium oxide.

Hydrated Lime. Of recent years the practice has grown, more particularly in the United States and on the Continent, of hydrating the lime mechanically at the limeworks. The process is carried out in machines called hydrators. The lime leaves the hydrator in the form of a fine powder, and is carefully sieved or air-separated to exclude unburned or unslaked portions. It has many points in its favour, chief among which are: (*a*) It can be stored indefinitely in bulk, or in bags without serious deterioration; (*b*) the danger of pitting in plaster is minimised by the removal of unslaked or unburnt particles; and (*c*) the period of tempering can be reduced from weeks or months to twenty-four hours.

Classification of Limes and Hydraulic Lime

The readiness and energy with which slaking is carried out together with the volume of powder furnished in this operation, and the subsequent hydraulic behaviour has been used as a means of classifying limes. Thus they are termed "fat" or "rich" if they slake rapidly and furnish a large volume of powder, and "lean" or "poor" if they are impure and slake slowly with little or no increase in volume.

The hydraulicity varies with the amount of active argillaceous matter contained, and they pass gradually from eminently hydraulic products containing 25 per cent. of active ingredients (silica and alumina) present, to feebly hydraulic products in which this content is as low as 10 per cent.

The following test was originally put forward by Vicat to distinguish between these classes, and also between hydraulic limes. The lime freshly burnt and broken to walnut size, is put into a cloth bag of open material or a basket, a volume of about a quart being used; and is immersed for not more than five seconds in pure water, then drained for a moment, and emptied into a stone or cast-iron mortar. The behaviour of the lime subsequently is closely observed: the lime may immediately begin to hiss, decrepitate, swell and give off steam, and at

the same time may fall to powder; there may be a period of inactivity of five minutes, after which the same phenomena may be observed: or only after fifteen minutes have elapsed, in which case the decrepitation and steaming are much less marked; a whole hour may elapse before a change is observed, when the action is again greatly moderated, so that but little heat is disengaged; or in extreme cases there may be no visible change for long periods of time.

As soon as the lime shows signs of breaking up, water is added carefully down the side of the vessel, the lime is stirred up with a spatula, and finally is worked up by a pestle to the consistence of a stiff clay, more water being added if necessary. It is then left for a couple of hours or until perfectly cold. The lime paste is then worked up again with the pestle, with the addition of more water if required, to the consistence of potter's clay, and sufficient is placed in a small pot or glass jar, of greater height than width, so as to fill it approximately two-thirds full. The lime is caused to settle down in the pot by striking the bottom of it on the palm of the hand or on a block, and the whole is then placed standing in a vessel of water so that it is immersed. Any change in consistence of the material is then observed over a considerable time.

The division of limes into Vicat's classes thus follows according to their behaviour during slaking and subsequent storing under water.

Fat limes slake rapidly and energetically and have their volume doubled, or more, in the process; their consistence remains sensibly the same after many years of immersion in water under the conditions of the test; and they dissolve practically completely in pure water frequently changed.

Lean limes slake slowly, with little or no increase in volume, and behave in water in a similar manner to the "fat" limes, except that they leave a residue devoid of any consistence on leaching with many changes of water.

Moderately hydraulic limes, set in fifteen or twenty days after immersion, and continue to harden; but after six or eight months the process becomes slow. After one year their consistency is about equal to that of hard soap. They dissolve in water with great difficulty (leaving an appreciable residue); the expansion on slaking is small.

Eminently hydraulic limes, set at some time between the second and the fourth day of immersion. After one month they are already very hard and altogether insoluble. At six months they appear like the absorbent calcareous stones, splintering under a blow and presenting a slaty fracture. The expansion on slaking is small.

It will thus be seen that the test of Vicat can be applied to all materials which lie between the limits of "fat" limes and eminently

hydraulic limes. The transition between these extremes is gradual, one class of material gradually merging into another. A certain amount of time is necessary in making the test, and it is not possible to express an immediate opinion as to which class a lime belongs. A chemical analysis will also give valuable information to an experienced observer, by indicating the proportion of argillaceous matter present, but is not conclusive in that it does not distinguish between silica and alumina which are inert, and silica and alumina which exert hydraulic activity.

As a guide Vicat's approximate figures of the proportions of inert and argillaceous matter present in the various types of lime may be given. Rich limes contain below 6 per cent. of inert foreign matter; lean limes contain below 30 per cent. of inert foreign matter; moderately hydraulic limes below 15 per cent. of clay as active ingredients; eminently hydraulic limes contain up to 25 per cent. of clay as active ingredient.

Testing of Limes

Until quite recently the methods employed in this country for testing limes were extremely crude. Within the last few years, however, notable improvements have been introduced as a result of research carried out by the Building Research Section of the Department of Scientific and Industrial Research. The bulk of this work has been conducted by Mr A. D. Cowper, under the present direction of Prof. R. E. Stradling, to whom the authors are indebted for their assistance in the preparation of this section. It is apparent from the varied classes of materials grouped together as limes, that a specification is desirable, in order that the buyer and user may be adequately assisted in obtaining the product required for any specific purpose, and for protection against inferior products. On this point Great Britain has lagged behind many other countries, in that a standard specification for lime has yet to be published. A step towards bridging this gap has been made by the Building Research Board, who have drawn up and published a series of tentative specifications.[1] These specifications have still to be adopted by the British Engineering Standards Association, by whom they are still under consideration. While it is possible that certain individual clauses may be modified, it is extremely improbable that any such modification will seriously affect the methods of testing, which are given on p. 304. For the purpose of comparison the specifications proposed in this country have been tabulated together with those of the United States and in South Africa.

[1] "Lime and Lime Mortars," A. D. Cowper, Building Research Special Report No. 9 (1927).

Quicklime (Chemical requirements)

	Great Britain (tentative).	United States.[1]		South Africa.[2]		
		Calcium Lime.	Magnesium Lime.	High Calcium Lime.	Calcium Lime.	Magnesium Lime.
Carbon dioxide	{ 5% max.[3] 7% ,,	3% max. 10% ,,	3% max. 10% ,, }	5% max.	5% max.	5% max.
Silica	...	...	...	2% ,,	5% ,,	...
Insoluble residue	3% max. on sample as received	...	...	...	...	...
Silica plus iron oxide plus alumina	...	5% max.	5% max.	...	...	...
Calcium oxide	...	75% min.	...	85% min.	80% min.	...
Magnesium oxide	...	...	20% min.	1% max.	...	30% max.
Calcium oxide plus magnesium oxide	75% min.	95% min.	95% min.	...	...	70% min.

[1] "United States Government Master Specification for Quicklime for Structural Purposes." Circular of the Bureau of Standards, No. 201 (Feb. 1925).

[2] "Standard Specification for Lime, 1926." South African Branch, British Engineering Standards Association, S.A., No. 3, 1926.

[3] The lesser value for carbon dioxide applies to materials sampled at place of manufacture. The higher value applies to materials sampled elsewhere.

The chemical requirements are important since they automatically preclude the use of unsuitable materials in the manufacture, or inferior methods of manufacture, or unsuitable methods of subsequent handling. Thus amounts of carbon dioxide in excess of that enumerated indicate an imperfect product which may be caused by insufficient calcination of the raw materials, or prolonged storage of the lime under unfavourable conditions, or a combination of both these factors.

As an alternative to a carbon dioxide determination, the loss on ignition may be determined by the method given below (see p. 307).

Chemical Analysis

(*a*) *Sampling of Quicklime and Hydraulic Lime.*—The specimen is emptied out on to a clean dry hard floor under cover, and, if necessary, broken by hammer or hand rammer until substantially all will pass through a 1-inch ring and no larger lumps are visible. The whole is then turned over by the spade three times, so as to mix thoroughly all parts, fine and coarse together. It is then worked into the form of a flat-topped circular pile and divided by the spade approximately into four equal quadrant-shaped sectors, the divisions made by the spade being carried down to the floor. Two diametrically opposite sectors are then discarded, care being taken to remove all the material, including fine dust, in this operation. The remaining two sectors of material are then mixed together thoroughly and the "quartering"

operation repeated: after discarding two quarters and mixing the remaining two as before, "quartering" is then carried out a third time if the material is still in considerable excess over the 25 lb. sample finally required. When what remains from these quartering operations is less than 50 lb. and still in excess of 25 lb., the final sample is taken by crushing the whole of this remainder to pass a No. 5 standard I.M.M. sieve and immediately placing it in a can which can be sealed; if the material is much in excess of 25 lb. at this stage, the 25 lb. sample required may be obtained by "dipping" with a metal scoop from the whole remainder, taking care to remove fine and coarse in the same proportion as it occurs in the mass. This is ensured by thorough mixing of the mass before the final sampling, and by scooping from the floor up so as to counteract the tendency of the fines to settle to the bottom of a pile.

For the purpose of making the test on the slaking properties of the quicklime, and on the putty resulting, the whole of the 25 lb. sample must pass a No. 5 standard I.M.M. sieve; two quantities, each of 5 kg. weight (approximately 11 lb.) are, in general, required for this purpose. Of the balance, a proportion is required for the chemical tests.

Sample for Chemical Analysis. For the purpose of chemical analysis and certain other tests, a representative small sample or samples are required. The preliminary sample may be taken by the "dip" method, using a small scoop or spatula after the manner indicated above, from the main 25 lb. final sample either just before enclosing the latter in its sealed can, or alternatively, immediately after removing the sample from its can and before commencing the tests to be performed with it. About 200 g. should be so taken and ground to pass a No. 10 standard I.M.M. sieve: this grinding is carried out in a porcelain mortar and must be done as expeditiously as possible. Then the final sample or samples, of approximately 50 g. each, for analysis are obtained by the "dip" method or by quartering down from this ground material, and must be sealed up immediately in a glass sample bottle with a well-waxed cork.

(*b*) *Sampling Hydrated Lime.*—Substantially the same general methods should be used as with quicklime, except that crushing and grinding are not necessary, and that a sampling tube may be employed for bags or barrels.

Sampling and grinding must be carried out as quickly as possible so that the material does not deteriorate through absorption of moisture and carbon dioxide. The total time occupied in mixing, quartering and preparation of the final samples should not exceed two hours (and with other than hard mountain quicklimes should not materially exceed half an hour).

Quicklime

The complete analysis of quicklime is carried out on similar lines to that of limestone. A prolonged agitation of the portion to be weighed out is inadvisable owing to the powerful affinity of lime for carbon dioxide and water. The sample should be ground to pass a No. 50 I.M.M. sieve. The analysis should not be conducted on the portion used for loss on ignition, owing to the bulky precipitate of calcium oxalate which would result from the use of 1 g. of material.

Method of Attack. 0·5 g. of sample which has been ground to pass a No. 50 I.M.M. sieve is heated strongly in a platinum crucible for twenty to thirty minutes.

Silica. After cooling the contents of the crucible are transferred as completely as possible to a platinum or porcelain dish and drenched with a small quantity of water. The dish is covered with a clock glass and 10 c.c. of hydrochloric acid slowly poured in. The platinum crucible is rinsed by warming with a few c.c. of 1 : 1 hydrochloric acid and the rinsings added to the dish, evaporated to dryness as far as possible on the water-bath, and then transferred to a hot plate, heated for one hour at 200° for calcium lime or 120° for magnesium lime. Ten c.c. of hydrochloric acid is added to the cooled mass and allowed to stand in a warm place for a few minutes, an equal bulk of water added and the dish transferred to the water-bath for ten minutes. Filter and wash twice with dilute hydrochloric acid and then with hot water until free from chlorides. Evaporate the filtrate to dryness, heat for a few minutes only and extract with hydrochloric acid as before. Filter through a separate paper. Combine both papers in a platinum crucible and ignite to constant weight. Add 5 c.c. of hydrofluoric acid and two drops of sulphuric acid. Evaporate to dryness and ignite for a few minutes. Cool and weigh. The loss in weight is recorded as silica.

Oxides of Iron and Aluminium are determined as on p. 339.

Calcium Oxide. The filtrate from the ammonia precipitate is evaporated to about 300 c.c., a few c.c. of ammonia added and 20 c.c. of a saturated solution of ammonium oxalate. The boiling is continued until the calcium oxalate assumes a granular form. The beaker is removed to a cool place for one hour. The clear liquid is poured through a filter and the precipitate washed three times by decantation. Any precipitate on the paper is rinsed back into the beaker and the calcium oxalate dissolved in dilute hydrochloric acid and the liquid diluted to about 100 c.c.

The lime is precipitated again as above, and after standing it is filtered through the previous filter and well washed with warm water. The precipitate is ignited to constant weight in a platinum crucible and weighed as lime (CaO).

Magnesium Oxide. The filtrates from the two lime precipitations are combined and evaporated to 250 c.c. and cooled. Ten c.c. of a 10 per cent. solution of sodium phosphate is added, and an appreciable excess of ammonia, and the whole well stirred. The beaker is set aside for twelve hours and the contents then filtered and washed three times with ammonia water. The precipitate is dissolved in a little dilute hydrochloric acid and then reprecipitated as above. It is filtered after standing about three hours and well washed with ammonia water and dried and ignited. It is weighed as magnesium pyrophosphate containing 36·2 per cent. of magnesium oxide.

Carbon dioxide is determined gravimetrically by the method of Fresenius (see p. 12). Five g. of sample should be taken.

Loss on Ignition. The loss on ignition is determined on a portion (of approximately 1 g. in weight) of the analytical sample of about 50 g. prepared in accordance with the method previously described, after further grinding to pass a No. 50 Standard I.M.M. sieve. The powder is introduced into a small crucible of a material which will be inert and invariable in weight under the treatment specified, and ignited in an oxidising atmosphere at a full yellow heat (about 1000° or above) for thirty minutes, using a means of heating which provides substantial immunity from sulphurous fumes (see p. 14). The crucible and contents are cooled in a desiccator in an atmosphere free from moisture and carbon dioxide, and weighed when cooled; the heating is then repeated for two successive periods of ten minutes each, the crucible being cooled in the desiccator as before and weighed between each heating period, and after the final heating. If the weight has remained constant to within 5 mg. during the two consecutive periods of ten minutes, the final weighing is taken as the correct value, and the "loss on ignition" is the difference between the original weight and the last weight, and is recorded as a percentage of the original weight. The "ignited portion" is then the difference between this and 100 per cent. If a difference in weight exceeding 5 mg. is recorded between two consecutive weighings, then the heating is continued for successive periods of ten minutes each until three consecutive weighings are the same to within 5 mg.

The fine grinding of the sample and weighings of the ignited lime must be carried out as expeditiously as possible, to avoid air-slaking: a dry stoppered weighing bottle should be used to enclose the crucible on each occasion.

Insoluble Matter. To approximately 5 g. of the analytical sample prepared in accordance with the method previously described, and ground to pass a No. 50 standard I.M.M. sieve, add 250 c.c. of 2 *N* hydrochloric acid. Stir to break up lumps, then heat to boiling, allow to stand ten minutes, then wash by decantation through a filter,

retaining the solid residue as far as possible in the original vessel. Wash back any residue from the filter to the original vessel with 5 per cent. sodium carbonate solution, using about 50 c.c. Boil, settle, and decant as before. Repeat the process with the 5 per cent. sodium carbonate solution. Finally, bring the residue on to the original filter, wash with water, then with dilute hydrochloric acid, and again wash with water until the washings are free from chloride. Ignite the filter paper and residue to constant weight.

Rapid Estimation of Lime. Either of the methods described for limestone may be applied (see pp. 299 and 300).

Determination of Free Lime.—(*a*) Lerch and Bogue's[1] Method. The proportion of "free lime" present may be determined by titration in a boiling solution of anhydrous glycerin in absolute ethyl alcohol, with a solution of ammonium acetate in absolute alcohol, using phenolphthalein as indicator as follows:—

The ethyl alcohol must be absolute, preferably distilled recently over metallic calcium and preserved in a well-stoppered bottle. The glycerin may be ordinary pure anhydrous glycerin. The phenolphthalein indicator should be about 0·2 per cent. solution in absolute alcohol. The ammonium acetate solution is made up with A.R. dry salt dissolved in absolute alcohol, about 16 g. per litre (approximately 0·2 N) and standardised against pure CaO: 0·1 g. of pure quicklime prepared by igniting A.R. pure precipitated calcium carbonate to constant weight, the determination to be made precisely according to the method described below. All reagents must be carefully preserved against absorption of moisture from the air.

0·2 to 0·5 g. (according to approximate CaO content) of the lime, prepared in accordance with the method described previously, and finely ground, is weighed out into a wide-mouthed flask of about 250 c.c. capacity, fitted with a double-bored rubber cork: a reflux air condenser with a calcium chloride guard-tube is fitted into one hole of the cork, while the jet of the burette containing the ammonium acetate solution can be introduced through the other hole, which is closed with a cork when not in use. Thirty c.c. of absolute ethyl alcohol, 6 c.c. of glycerin and a few drops of phenolphthalein are added, and the mixture is heated to boiling and kept boiling steadily under the reflux condenser. From time to time the boiling is interrupted and the ammonium acetate solution added cautiously, until the pink colour does not reappear on the boiling for several minutes, the final occasion for thirty minutes. The amount of free lime present is then calculated from the amount of ammonium acetate solution consumed and the strength of the solution. The total time required for the completion of a test may vary from a few minutes to an hour or more,

[1] *Ind. Eng. Chem.*, 1926, 18, 739.

depending on the amount of free lime present, the fineness of grinding and other factors.

(*b*) South African Standard Specification. As an alternative to the above method the following procedure may be adopted. The sample is crushed as rapidly as possible, until it is sufficiently fine to pass through an I.M.M. standard 60-mesh linear screen (aperture 0·0083 in.), but actual sieving should be avoided. It is then returned to the receptacle so as to prevent any unnecessary exposure to the air.

The whole sample is spread out in a layer about half an inch thick on glazed paper and rather more than 2 g. dipped out from a number of points in small quantities. This small amount is reduced to an agate mortar to a fine powder free from grit. Two g. of this is carefully weighed out and agitated with 1 litre of a 2 per cent. cane sugar solution free from carbon dioxide or 1 g. with 500 c.c. of 2 per cent. sugar solution. If a shaking machine is available, two hours' continuous agitation should be given; if not, three hours' intermittent agitation, *i.e.*, shaken not less frequently than once in five minutes, every care being taken to prevent coagulation of the lime.

When the agitation is finished the solution is filtered, rejecting the first 100 c.c. of filtrate, or allowed to settle until clear and aliquot portions titrated with $N/10$ or $N/5$ acid, using rosolic acid as indicator, avoiding delay so as to obviate undue exposure to the atmosphere.

Hydraulic Lime

Providing the proportion of insoluble matter (silica, alumina, etc.) does not exceed 25 per cent., the methods detailed for quicklime can be followed. Where this limit is exceeded about 0·5 g. of sodium carbonate must be mixed with the material before the initial ignition. The procedure is then as described for quicklime.

Hydrated Lime

The complete analysis of hydrated lime is carried out exactly like that of quicklime. In addition a determination of the mechanical moisture must be made as a check on the efficiency of the hydrating process.

Free Water. The determination should be carried out in the apparatus illustrated in Fig. 48. About 25 g. of the material is introduced into the glass tube T, which is sufficiently large to enable the lime to be spread out in a comparatively thin layer. The drying train consists of a tower A, containing calcium chloride, and a U-tube B containing soda lime. It allows only dry air, free from carbon dioxide, to pass over the material. The U-tube C contains calcium chloride, and is inserted to prevent moisture from the aspirator coming in contact with the lime. The whole train may be

conveniently erected so that the tube T passes through a small air bath. The tube is heated for two hours at 100° to 105° while dry air is drawn over the material. After cooling, the tube and contents are re-weighed. The loss in weight represents free moisture.

Combined Water. This is found by difference between the loss on ignition (see method for lime) and the combined results for the carbon dioxide and mechanical moisture. The result is sufficiently accurate for practical purposes.

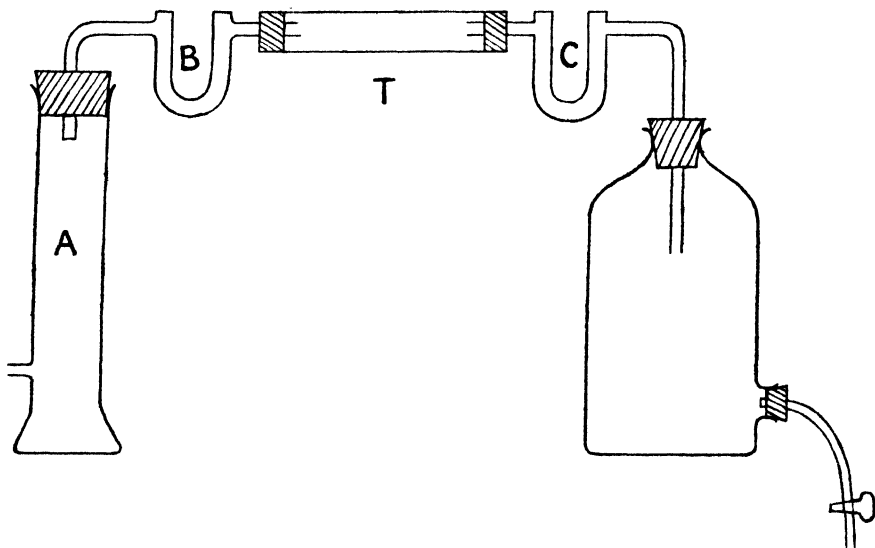



Fig. 48.

Physical Tests

Burnt lime is not used as such in building operations but is invariably slaked before use, and then mixed with sand and hair, etc., to form a plaster. Plaster is rarely called upon to sustain any great load, but has certain other requirements to conform with, of equal importance. Thus the inert residue remaining after slaking should not be excessive; the volume yield on slaking is important as a guide to the purity and degree of burning the material has received; a certain standard of plasticity of the material is desirable from the point of view of the user; and finally, the degree of hydraulicity is important as indicating the ultimate hardening properties of the plaster.

It is well recognised that the volume yield of a lime on slaking is, within certain limits, dependent on the amount of water used. For this reason, in order to reduce any tests to a comparative basis, it is necessary to adopt a standard method of slaking. The method in

use at the Building Research Station is that known as "Isothermal Slaking." A general discussion of this method is to be found in the work of Cowper and Williams.[1]

Isothermal Slaking of Lime. The sample of quicklime is crushed to pass a No. 5 standard I.M.M. sieve, and is slaked "isothermally" by immersion in water maintained at a substantially uniform temperature during the actual slaking process, in accordance with the following general method, this temperature being maintained within about 2° of that specified for the particular lime. Where no temperature has been specified, duplicate isothermal slakings should be carried out on two similar samples at the temperature of 50° and 100° respectively, and both results fully reported as to residue on slaking, density of putty, volume yield, plasticity and rate of settling, but mechanical strength, hydraulicity and soundness tests respectively should be carried out (unless otherwise specified, as in isolated cases) only on the one putty specimen prepared in accordance with this method, that specimen being chosen which exhibits the higher volume-yield; in such cases, the other specimen of putty can be omitted from the latter three tests.

Twenty kg. of water (or up to 40 kg. for certain mountain limes of high volume-yield) is placed in the slaking vessel and adjusted to within 2° of the specified isothermal slaking temperature, as indicated on the thermograph connected. While stirring rapidly, a weighed quantity of 5 kg. of the quicklime is slowly added, by cautious shaking from a scoop only partially filled, at such a rate that (*a*) not less than five minutes is required to introduce the whole; (*b*) that the specified slaking temperature can be maintained within about 2° by aid of the cooling means provided (a stream of water at a somewhat lower temperature, etc.); (*c*) that the mass does not boil over in the case of rapid-slaking limes, and the danger of local superheating is obviated. If any water is added, this must be done slowly and in a fine spray or stream to avoid excessive local chilling. If the temperature of the whole tends to fall below the specified isothermal slaking temperature, the means of heating provided is utilised to maintain it within 2° of the latter temperature. After the violent slaking action, if any, has subsided, the temperature of the whole is maintained substantially constant at the specified temperature for a period of one hour reckoned from the commencement of the slaking. The whole is then allowed to stand in the laboratory for twenty-four hours, attaining approximately the laboratory temperature in the process; it is thoroughly stirred with a wooden stirrer at least twice during this period, the last time not less than one hour before the expiration of the twenty-four hours named.

[1] *J. Soc. Chem. Ind.*, 1928, 47, 31 T.

Residue on Slaking. After the expiration of twenty-four hours, reckoned from the time of the commencement of the slaking, first the supernatant liquid, and then the remainder, after having been thoroughly stirred with a wooden stirrer, is passed through a sieve or sieves into a similar vessel fitted with a temporary lining composed of a rectangular sheet of unbleached calico about 4 ft. by 6 ft., care being taken that the whole of the contents of the former vessel are transferred on to the sieve or sieves: for this purpose the former vessel should be washed out with a jet of water. The sieves should be standard No. 20 I.M.M. and/or No. 50 I.M.M. as specified for the type of lime under test: where both sieves are used, they should be nested one above the other on the supports provided for this purpose in the order named.

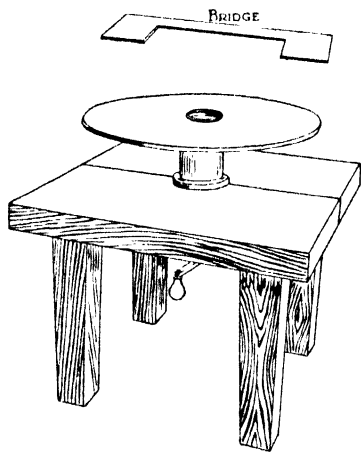



Fig. 49.

The residue on the sieve or sieves is then washed by a moderate jet of water from a rubber pipe, the whole operation taking, in all, not over thirty minutes. The residue must not be rubbed through the corresponding sieve. The residue on each sieve is then dried to constant weight at 110°, and recorded as "Residue on Slaking," calculated on the weight of quicklime taken.

Preparation of Lime Putty. The ends of the sheet of calico are then folded together to form a bag, and this is tied up and suspended by a cord to allow the lime putty to drain; the bag may be subjected to moderate pressure by the hands to accelerate this process.

(*a*) Lime putty prepared from quicklime. The consistence of a portion of the putty prepared as above, sufficient in quantity for the purposes of the tests for volume-yield, plasticity and soundness is adjusted to the standard value of half-inch slump when tested in the Southard Viscosimeter.

The Southard Viscosimeter. This apparatus is illustrated in Fig. 49. It consists of a vertical metal cylinder, 2 in. in internal diameter, equipped with a tight-fitting metal piston having a working stroke of 2½ in. measured from the upper end of the cylinder. The piston can be raised, without rotation, by a coarse thread screw having four threads per inch, passing through a nut at the lower closed end of the cylinder and engaging the piston on the lower side of the latter. In operation, the piston is lowered to the bottom of its stroke, the cylinder

is filled carefully with the putty, avoiding the inclusion of air-bubbles, and the putty is struck off smoothly at the top. The piston is then raised steadily by rotating the screw at the rate of one turn per second for ten seconds, thus ejecting the contents of the cylinder vertically upwards. With lime putty, the degree to which the ejected cylinder of putty has slumped is then determined by measuring its present height, by means of a metal bridge or similar device : for this purpose the top of the cylinder is provided with an external horizontally extended flange with a plane surface on which to apply the bridge. For use with gypsum plasters, this surface is etched with concentric rings spaced at a radial distance of 1 cm. for convenience in measuring the spread.

Care should be taken during the ejection of the putty that no vibration is imparted to the viscosimeter and that it is standing firmly on all four legs. The apparatus must be thoroughly washed out between each determination.

The constants of the Southard viscosimeter are as follows : diameter of metal cylinder, 2 in.; stroke of piston, 2½ in.; actuating screw, four threads per in., with handle at lower end ; piston to be raised (without rotation) by one turn of the handle per second for ten seconds; bridge to check amount of slump, with 2 in. clearance. *Slump of putty for "Standard Consistence" : ½ inch* ± $\frac{1}{16}$ (i.e., *from* 2½ *in. to* 2 *in. in height when ejected*). Concentric rings with radial distance of 1 cm. are etched on the flange.

About 260 c.c. of putty is accordingly knocked up, thoroughly worked and mixed, with as little loss as possible in the process. A convenient means for this purpose is a small pugmill of the domestic mincing machine type, the material being passed through twice on each occasion of use, and care being taken to clean out the dead spaces each time.

The piston of the Southard viscosimeter is lowered to the bottom of its stroke, which should correspond to ten complete turns of the handle from the position where the top of the piston is flush with the top of the plate. (Any dried and caked lime or plaster under the piston will tend to limit the stroke and produce erroneous slump figures.) The cylinder is then filled carefully with the knocked up and well-mixed putty, avoiding the inclusion of air-bubbles by placing in small quantities at a time and working each addition well down before adding the next. The putty is then struck off smooth at the top and flush with the surface of the plate by means of a trowel or spatula. The surface of the plate round the cylinder-rim should be clean after this operation.

The viscosimeter should be placed on a firm table with the plate precisely horizontal, and resting firmly on all four feet. The piston is then raised steadily and at a uniform rate by rotating the screw by means of the handle, at the rate of one turn per second for ten seconds, rising therefore 2½ in. in this time and ejecting the contents of the

cylinder vertically upwards. The degree to which the ejected cylinder of putty has slumped is then determined by applying the metal bridge in a vertical position straddling the putty and with the legs resting on the plate. The bridge should be applied on several diameters, so as to obtain an average indication of the amount of slump, on account of an occasional tendency towards an uneven slump.

If the observed slump departs from the standard amount of ½ in. by more than $\frac{1}{16}$ in., the putty is removed and the water content of the whole portion adjusted by (*a*) withdrawing water by placing for a few minutes on a clean dry porous slab, where the slump was excessive, or (*b*) adding a small quantity of clean water and incorporating it by thorough knocking up with the trowel, where the slump was deficient. The whole portion is then passed twice more through the mincing machine, with the same precautions as before, and the slump tested again on the viscosimeter. If the slump is still incorrect, the whole process is repeated, and the adjustment of water content continued until the correct value is obtained within the given limits. This putty is then available for subsequent tests.

It is essential that as little of the lime putty as possible be lost during cleaning the apparatus, since all may be required for subsequent tests, and considerable errors may be introduced, *e.g.* in the strength tests by loss at this point. It is obvious that in knocking up the putty for each determination, that left in the "dead" spaces of the mincing machine must be scraped out carefully and added to the main portion.

(*b*) Putty prepared from dry hydrated lime. The consistence of lime putty prepared from dry hydrated lime is adjusted to the same standard value of ½ in. slump when tested in the Southard viscosimeter, and in the same manner as that defined in the first part of this clause for lime putty prepared from quicklime.

A convenient quantity (5 kg. when further tests are to be applied) of the dry hydrate is mixed with sufficient clean water to give a plastic mixture, and this is stored in a covered vessel at ordinary room temperature for not less than sixteen hours and not more than twenty-four hours before finally adjusting the consistence and testing. About 260 c.c. of this putty is then taken and treated in the manner described on p. 313.

The adjustment of consistence should be completed within thirty hours of the commencement of the slaking process, or of the first addition of water to dry hydrate respectively.

Determination of Volume-Yield

The volume-yield of lime putty should be determined from the density of a portion of the putty which has been adjusted to the standard consistence in accordance with the method previously given. The density of the putty is determined in the customary manner by

measuring the weight of a known volume of the putty, a vessel of the shape and dimensions shown in Fig. 50 being used for this purpose, care being taken to eliminate air bubbles. The determination of density should be carried out in duplicate, the higher figures being taken for the purposes of the calculation in the case when the two

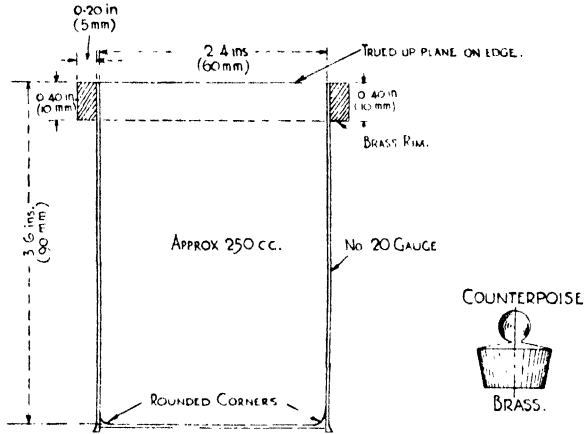



FIG. 50.—LIME PUTTY DENSITY VESSEL.

Tinned Iron Cylindrical Pot 2·4 ins. (60 mm.) diameter by 3·6 ins. (90 mm.) deep with soldered joints and with reinforced rim of brass, the upper edge made plane. Brass counterpoise adjusted to equal weight.

results for the density are not identical. Then if d = density of putty so determined, the volume-yield in c.c. per g. of quicklime is calculated from the formula

$$\text{Volume-yield} = \frac{0.70}{d - 1}.$$

The volume-yield in cubic yards per ton (2240 lb.) is given by multiplying the above result by $1\frac{1}{3}$.

TABLE OF VOLUME-YIELDS

Giving volume-yield in c.c. of lime putty of standard consistence per g. of quicklime taken, if density of putty = d.

Density d.	Volume-Yield $\frac{0{\cdot}70}{d-1}$	Density d.	Volume-Yield $\frac{0{\cdot}70}{d-1}$	Density d.	Volume-Yield $\frac{0{\cdot}70}{d-1}$
1·20	3·50	1·32	2·19	1·44	1·59
1·21	3·33	1·33	2·12	1·45	1·56
1·22	3·18	1·34	2·06	1·46	1·52
1·23	3·04	1·35	2·00	1·47	1·49
1·24	2·92	1·36	1·94	1·48	1·46
1·25	2·80	1·37	1·89	1·49	1·43
1·26	2·69	1·38	1·84	1·50	1·40
1·27	2·59	1·39	1·79	1·51	1·37
1·28	2·50	1·40	1·75	1·52	1·35
1·29	2·41	1·41	1·71	1·53	1·32
1·30	2·33	1·42	1·67	1·54	1·30
1·31	2·26	1·43	1·63	1·55	1·27

The volume-yield of a lime putty should not be less than 1·7 c.c. per g. ($2\frac{1}{4}$ cu. yd. per ton).

Determination of Plasticity (Working Time)

The plasticity of a plaster from the user's standpoint is of considerable importance and may be generally defined as that quality which makes it easy to work and spread. It is extremely hard to apply a quantitative test to this property, and research workers have devoted many years to the development of a machine capable of expressing numerical results and so obviating personal judgment.

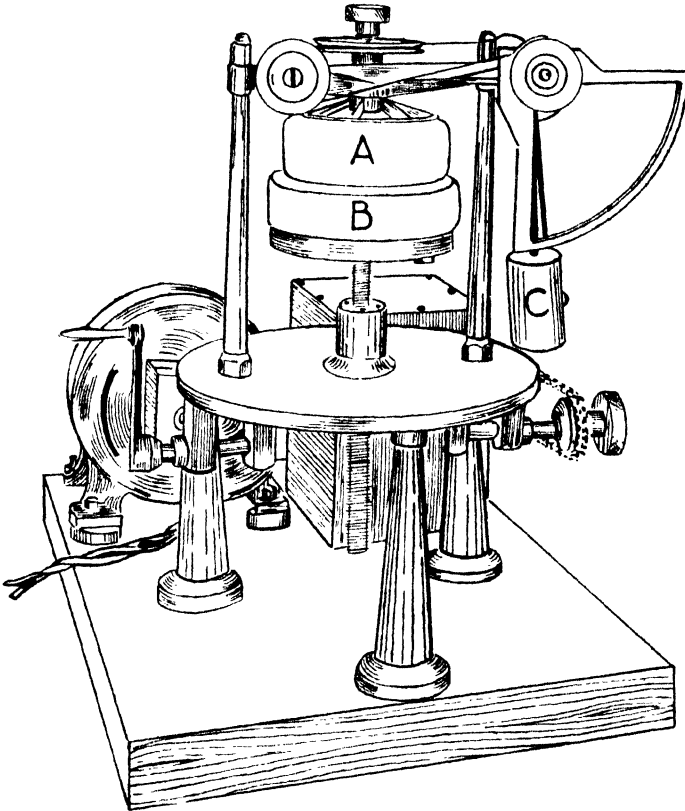



FIG. 51.

The instrument detailed below and favoured by the Building Research Department is that developed by Emley of the United States Bureau of Standards.[1] It is based on the principle that the material is most plastic which is most capable of retaining water against the suction of a surface to which it is applied, and that a material is more plastic which requires less work to spread it.

The Emley plasticimeter is illustrated in Fig. 51. It is a machine

[1] *U.S. Bureau of Standards*, Technical Paper No. 169, 1920.

having a turntable which has a slow vertical motion while it rotates, carrying a standard porous plaque of unglazed porcelain, immediately above which is mounted a circular disc or trowel, rotatable freely in bearings on a vertical shaft but immovable vertically, and connected mechanically to a pendulum carrying an indicator which moves over a circular scale graduated up to 100 divisions, in such a manner that the torque applied to the trowel-disc in the operation of the machine is opposed by and measured in terms of the movement of the pendulum bob. The lime putty is cast in the form of a circular cake on the standard porous plaque, and after adjustment in the machine, is compressed between the trowel-disc and the slowly rising and rotating plaque: the resulting torque on the trowel-disc, due to the viscous resistance of the putty, is read on the circular scale.

The standard porous plaque of unglazed porcelain is 11 cm. in diameter and 24 mm. thick, with a uniform porosity corresponding to an absorption of 90 g. of water at room temperature when dried completely at 110° and then completely immersed in water at room temperature for two hours, with an absorption of 75 g. when dried completely and then laid in water ½ cm. deep for three minutes: with a permissible deviation of 3 g. from those figures in either direction.

The trowel-disc is of polished metal and 76 mm. in diameter. The speed of revolution of the turntable is one revolution in six minutes four seconds; the vertical rise of the same is 2 mm. per revolution. The torque on the disc is 14·400 g. cm. The mould for the cake of putty is a split metal ring 80 mm. in diameter and 40 mm. high.

The lime putty, adjusted to standard consistence in accordance with the method given on p. 312, is fitted into the mould while resting on a non-porous plate in such a manner as to exclude air bubbles and smoothed off level with the upper edge of the mould with a spatula. At a given time (termed zero time) a previously cleaned and dried standard porous plaque is placed over the mould, and the latter quickly inverted and the non-porous plate (now uppermost) withdrawn. The mould is then removed from the cylinder of putty by lifting it vertically, with the assistance of a loosely fitting piston of wood which is rested on the top of the putty during the process; the putty is then lightly smoothed off after removal of the mould and wooden piston, if necessary, by means of a smooth metal spatula and immediately introduced in the machine.

The porous plaque is placed in position on the turntable and the latter rapidly raised until the trowel-disc presses firmly and uniformly on the whole surface of the top of the cake of putty, but without unnecessarily disturbing the latter. The driving mechanism of the machine is then started. The time elapsing between zero time and

the moment of starting the machine should not sensibly exceed one minute. The torque reading on the scale is then observed every fifteen seconds, and the time observed between zero time to the point where either (*a*) the torque reading attains 100 on the scale, or (*b*) any reading is less than the one before (when the cake of putty will exhibit definite signs of rupture, further than mere superficial cracks at the edges), whichever time is the less: this time is termed the "working time," and a measure of the plasticity of the putty.

After each determination the standard porous plaque should be thoroughly cleaned and immersed in 20 per cent. hydrochloric acid for a period of at least six hours, followed by immersion in clean running water for at least eight hours, and dried to constant weight at 110°. By means of this machine it is possible to classify limes in groups according to the time required to bring about a rupture, and each class may be further subdivided according to the work expended in spreading them during this time. The longer the time and the less the work, the higher the practical plasticity of the material.

The plasticity or working time obtained thus should be not less than seven minutes, but if required a greater time may be set.

Rate of Settling of Lime Suspension

The rate of settling of a dilute suspension of lime hydrate is determined by observing the rate of fall in fifteen minutes of the upper surface of the solid suspended matter in such a suspension, containing approximately the equivalent of 10 per cent. by weight of dry hydrated lime; with lime putty, such an amount that will be equivalent to approximately 7·57 per cent. by weight of quicklime.

A. *Lime Putty* (prepared from quicklime). The approximately 7·57 per cent. suspension prepared from lime putty is made by adding to a sufficient quantity (about 20 g.) of the lime putty, when adjusted to standard consistence in accordance with the method given, a quantity of distilled water calculated from the weight and density of the putty sample according to the following method: the quantity of water to be added is obtained by multiplying the weight of the putty taken by the factor n, where

$n = 17.92 - \frac{18.92}{d}$ (d = density of lime putty, determined in accordance with Method No. 7, p. 314).

The suspension is prepared within thirty hours of the commencement of slaking. The water should be added to the putty slowly, and the whole thoroughly mixed and stirred so that an even suspension devoid of lumps is obtained.

B. *Dry Hydrated Lime.* The 10 per cent. suspension of hydrated lime is prepared by soaking a convenient quantity (about 20 g.) of the dry hydrate in nine times its weight of distilled water at the ordinary room temperature in a covered vessel for a period of not less than sixteen nor more than twenty-four hours, and thoroughly stirring before use. After thorough agitation about 50 c.c. of the suspension shall be poured into the settling apparatus as quickly as possible. The time is observed immediately the suspension has been introduced and the level adjusted to zero on the scale; the distance settled after fifteen minutes is then observed. The rate of settling is recorded in mm. settled in fifteen minutes.

The settling apparatus consists of a vertical glass tube of uniform bore, fitted with a tap at the lower end and provided with a millimetre scale. The tube shall be not less than 40 cm. in length and not less than 1 cm. and not more than 1·5 cm. in diameter; an ordinary 50 c.c. burette is suitable.

TABLE OF WATER-RATIOS: STANDARD RATE OF SETTLING TEST

Giving weight of water required to make a suspension of approximately 7·57 per cent. of quicklime, or 10 per cent. of lime hydrate, when mixed with unit weight of lime putty of standard consistence, of density = *d*.

Putty Density *d*.	Value of Factor $17 \cdot 92 - \frac{18 \cdot 92}{d}$. G. water per g. lime putty.	Putty Density *d*.	Value of Factor $17 \cdot 92 - \frac{18 \cdot 92}{d}$. G. water per g. lime putty.	Putty Density *d*.	Value of Factor $17 \cdot 92 - \frac{18 \cdot 92}{d}$. G. water per g. lime putty.
1·20	*Add* 2·15	1·32	*Add* 3·59	1·44	*Add* 4·79
1·21	2·29	1·33	3·70	1·45	4·87
1·22	2·42	1·34	3·80	1·46	4·96
1·23	2·54	1·35	3·91	1·47	5·05
1·24	2·67	1·36	4·02	1·48	5·14
1·25	2·79	1·37	4·12	1·49	5·23
1·26	2·92	1·38	4·22	1·50	5·31
1·27	3·04	1·39	4·32	1·51	5·40
1·28	3·15	1·40	4·41	1·52	5·49
1·29	3·26	1·41	4·51	1·53	5·57
1·30	3·37	1·42	4·60	1·54	5·64
1·31	3·48	1·43	4·70	1·55	5·72

Sieve Analysis of Hydrated Limes

100 g. of the sample is washed with a jet of water on Nos. 20, 50, and 200 standard I.M.M. sieves in that order, the sieves being superimposed on one another and each being removed in turn after the length of time specified for washing on that sieve has elapsed. The jet of water is obtained by compressing with the fingers the end of a piece of rubber tubing of approximately ¼ in. internal diameter through which is passing a moderate flow of water.

The washing on the No. 20 sieve is continued for three minutes, after which this sieve is removed and the washing continued on the No. 50

sieve for a further three minutes; then in succession the No. 50 sieve is removed and the washing continued on the No. 200 sieve for a further five minutes, making a total time of fourteen minutes. The residues on each sieve are weighed after drying to constant weight at 110°, and the percentage of the original weight of hydrated lime taken recorded. In recording the results of the test, the following method is used. If a = residue on No. 20 sieve; b = residue on No. 50 sieve; c = residue on No. 200 sieve; then recorded,

"Total Residue on No. 20" = a
"Total Residue on No. 50" = $a+b$
"Total Residue on No. 200" = $a+b+c$.

III.—LIME-SAND MORTAR

Consistence of Lime-Sand Mortars.—It is well recognised in the testing of lime-sand mortars for tensile strength, etc., that changes of consistency of the original mix have an important bearing on the ultimate strength of the set mass. Hence it is desirable to adopt a standard consistence for testing purposes. For lime-sand mortars, the method favoured in this country is the flow table method.

The flow table was first developed in the United States[1] for measuring the consistence of concrete, and as the name suggests, the method consists in measuring the flow or spreading out of a plastic mass, when subjected to deforming forces.

The apparatus is illustrated in Fig. 52. It consists essentially of a horizontal flat smooth steel table, 15 in. in diameter and $\frac{3}{16}$ in. thick, mounted on a vertical shaft which may be raised and then allowed to fall freely by a cam, the fall being exactly $\frac{1}{2}$ in. The total weight of the moving part, table, shaft, etc., which is free to fall is 10 lb. The length of fall is defined by a pin fixed through the shaft coming into contact with the supporting frame, the contact being therefore steel on steel.

The consistency test of sanded lime mortars is carried out on the flow table according to the following method:—

A. *From Quicklime.* The mortar is prepared from lime putty resulting from standard isothermal slaking (see method on p. 311) by mixing substantially the whole of the putty prepared from 5 kg. of quicklime with 15 kg. of standard sand, as much as possible of the small portion of putty used for the determination of plasticity, volume-yield, etc., being returned to the main portion for this purpose. The adjustment of consistence is made immediately after completion of the volume-yield and plasticity tests and recovery of the small portion of

[1] *Concrete*, 16, 274; *Proc. Amer. Soc. Test. Mats.*, 1921, p. 983.

putty used in the latter tests, and within forty hours of the commencement of the slaking operations.

B. *From Dry Hydrated Lime.* The mortar is prepared from the lime putty made from the dry hydrate in accordance with the method given on p. 314, by mixing a known weight (5 kg.) of the dry hydrated lime with sufficient water to give a plastic mixture, and storing in a covered vessel at ordinary room temperature for not less than sixteen hours and not more than twenty-four hours; then mixing substantially the whole of this putty with an amount of standard sand calculated in the following manner from the weight of the dry hydrate. Weight of

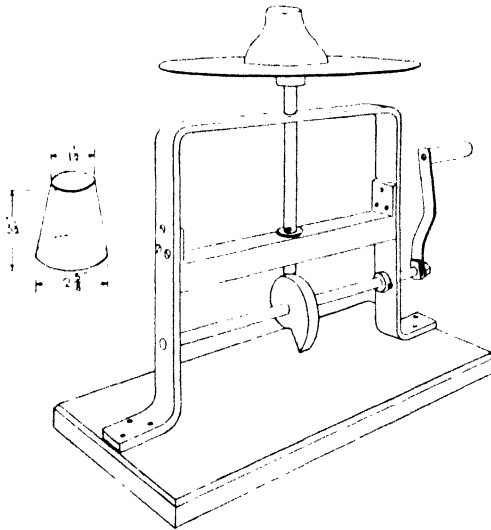



FIG. 52.—FLOW TABLE.

Table, 15 ins. diameter. Fall, ½-in.: stop, steel on steel. Weight of moving parts, 10 lb. Number of Falls, 20. Thickness of plate, $\frac{3}{16}$ in.

sand taken = 3 × "per cent. of 'Ignited Portion'" × weight of dry hydrate: where the "per cent. of 'Ignited Portion'" is determined in accordance with the method on p. 307, being the difference between the "per cent. Loss on Ignition" and 100 per cent.

The standard sand employed is that defined in the current B.E.S.A. Standard Specification for Portland Cement, Clause II (see p. 361).

Gauging. Immediately before testing the consistence, the lime putty and standard sand in the specified quantity is thoroughly mixed for five minutes with the trowel on a clean non-porous surface. The adjustment of consistence is made by adding small quantities of water, or by withdrawing water by placing the gauged mass for a short time on a clean dry porous slab (drying table) respectively. The consistence is tested by subjecting a truncated cone of the mortar originally 3½ in.

in height and $1\frac{1}{2}$ and $2\frac{5}{8}$ in. in diameter at the upper and lower ends respectively to twenty bumps of $\frac{1}{2}$ in. each on the flow table. The mortar cone is prepared from a portion of the mortar in the following manner:—

A bottomless metal mould of the prescribed internal dimensions and shape is placed narrow end down on a small glass plate, and is filled with the mortar by ramming the latter in small portions lightly into position with the fingers so as to eliminate air bubbles. After striking off the surplus level with the upper end with the trowel a larger glass plate is placed on the latter, and the mould is inverted and placed on the middle of the flow table: the glass plates are then carefully withdrawn. By cautiously withdrawing the mould and assisting if necessary by light downward pressure with the finger on the small end, the cone of mortar is left unsupported on the table, ready for the test.

The spread of the mortar mass on the flow-table is measured on several diameters, and the mean spread taken: standard consistence is indicated by a mean spread of 4 inches $\pm \frac{1}{8}$ in. The adjustment of consistence is repeated until this standard is attained and should be completed within thirty hours of the first addition of water to dry hydrate.

When preparing sanded lime mortars from the lime putty resulting from isothermal slaking of 5 kg. of quicklime in accordance with the method given, or prepared from a definite weight (5 kg.) of dry hydrated lime, a small amount of the putty will, in general, have already been consumed in mechanical losses during adjustment of consistence, determination of plasticity and volume-yield, and in transference in the several operations: great care should accordingly be taken to render these losses as small a proportion of the whole as practicable, in order not to affect sensibly the 3 : 1 sand ratio based on the original weight of the lime.

MECHANICAL TESTS

(*a*) Preparation of Test Specimens

Tensile Strength. — The tensile strength is determined on briquettes of the shape and dimensions substantially as specified in the current British Engineering Standards Association Standard Specification for Portland Cement (see p. 358). The briquettes are prepared in the following manner:—

A mixture of slaked or hydrated lime and standard sand is made in a proportion equivalent to approximately one part by weight of "lime" to three parts by weight of standard sand. After adding the specified quantity of sand, the mortar is thoroughly mixed with a

trowel on a clean non-porous surface for five minutes, and then the water content is adjusted to the standard consistence for sanded mortars, *i.e.*, to a standard spread of 4 in. on the flow table after twenty falls through ½ in. The mortar is thoroughly mixed after each adjustment of consistence.

The briquettes are prepared in moulds to the form required to produce the shape and dimensions indicated, each mould resting upon a non-porous plate. The mortar is placed in the moulds in three layers, each consecutively pressed down and consolidated into a uniform mass by pressure with the thumbs. The third layer should be more than sufficient to complete the filling of the mould and provide an excess of approximately ¼ in. in thickness above the surface of the mould. The mass is then subjected to a pressure with the gauging trowel sufficient to level the same to the surface of the mould, the excess of mortar being accordingly squeezed out in the process between the trowel and the top of the mould. The briquettes are finished off in the mould by smoothing the surface with the blade of a trowel or spatula. No other implements nor any mechanical means of ramming should be used in filling the moulds. The test briquettes should be prepared within thirty hours from the time of commencement of slaking, or first addition of water to dry hydrate, respectively.

The formula given on p. 321 for the calculation of the proportion of standard sand to be added to the putty prepared from dry hydrated lime is devised to give a sand-ratio corresponding approximately to 3 : 1 by weight referred to the weight of the quicklime from which the dry hydrate was prepared, and thus to place the dry hydrate on a par with quicklime in this test.

In comparing quicklime and dry hydrated limes this formula actually gives a slight advantage to dry hydrated limes in the matter of relative richness of the mortar-mix, in the proportion to which the quicklimes have become air-slaked before being tested; but this should be relatively insignificant in practice.

Compressive Strength.—The compressive strength is determined on test specimens made of the same 3 : 1 mortar, and prepared in a precisely similar manner to that used in forming the tensile strength briquettes.

The test specimens shall be made in the form of cylinders 2 in. in diameter and 4 in. high, prepared in split metal cylindrical moulds of those dimensions, and in accordance with the following method:—The 3 : 1 sanded mortar, after thorough mixing and adjustment to standard consistence as on p. 320 shall be placed in the mould in six layers, with the mould resting on a non-porous plate. The first five layers (sufficient to fill the mould to within about ¼ in.

of the top) shall be tamped down consecutively, with the aid of a compactor, consisting of a light cylinder of wood about ¾ in. in diameter and 6 in. long. Special care should be taken that the parts near the side of the mould receive thorough consolidation. The sixth layer shall then be added and shall provide an excess of about ¼ in. above the top of the mould, and after being consolidated with the mass by the thumbs, this excess shall be squeezed off level with the top of the mould with a trowel. The surface shall then be smoothed off with a spatula. No other implements than the compactor, the trowel and spatula shall be used in filling the moulds. The test pieces should be prepared within thirty hours from the commencement of the slaking, or first addition of water to dry hydrate, respectively.

Storage of Test Specimens.—The test specimens are stored in their moulds in an atmosphere saturated with water vapour at room temperature for not less than twelve and not more than eighteen hours, and are then placed in a well-ventilated oven maintained at a temperature of 37° for six hours. They are then removed from the moulds, placed in metal trays and covered with dry sand to a depth of approximately 1 in. and, in succession, with a layer of dry powdered hydrated lime at least ¼ in. in depth. The hydrated lime should be renewed for each test, and at least every month during longer periods of storage. The loaded trays are stored at ordinary room temperature.

At the expiration of seven, fourteen, twenty-one, or twenty-eight days, in accordance with scheme of test from the time of gauging a proportion of test specimens shall be removed from the dry sand storage and immediately submerged in clean fresh water. In this operation each tensile briquette should be placed carefully by hand in the bottom of a metal tray, and resting symmetrically on two parallel cylindrical glass rods ½ in. in diameter and placed 2 in. apart, so that each briquette is supported clear of the bottom and sides of the tray, and of every other briquette. Water is then run in gently in such a manner that no briquette receives the direct force of the stream, and until all briquettes are submerged to a depth of approximately 1 in. The tray should not be disturbed after the briquettes have been submerged, nor should the water be agitated in any manner. Compressive strength specimens may be simply laid on their side in the bottom of the tray. The temperature of the water during the test should be maintained between 14° and 20°.

Hydraulicity Test. (Qualitative: 28-day specimens only.) Twenty-four hours after the moment of immersion of the tensile briquettes they shall be carefully examined in a good light without disturbing them in any way, for signs of collapse or disintegration.

(*b*) Method of Testing

Tensile Strength Test.—At definite periods, seven days, fourteen days, twenty-eight days, three months, six months, or one year, etc., in accordance with scheme of test after the time of gauging the briquettes are removed from storage, dry or wet, and tested for breaking strength. The breaking strength is the average tensile strength of six briquettes. The briquettes to be tested are held in strong metal jaws of the shape substantially as shown in the current B.E.S.A. Standard Specification for Portland Cement, and the load steadily and uniformly applied, starting from zero, and increased at a rate not exceeding the rate of $\frac{3}{4}$ lb. per sq. in. of section per second.

Briquettes withdrawn from wet storage are tested immediately and whilst still wet; briquettes which have been stored exclusively in dry sand are transferred to a metal tray and covered to a depth of 1 in. with fresh quicklime on the penultimate day, and withdrawn from this and tested dry on the last day of the period in question.

In breaking briquettes on the small testing machine the following conditions are to be observed:—

(1) The lever system shall be balanced when the empty shot receiver is suspended from the lever.

(2) The load shall be applied at the rate of 9 lb. in twelve seconds.

(3) The balance on which the load is weighed shall be brought exactly to zero by the weight of the empty can.

(4) The readings on the balance give the true breaking strength in lb. per sq. in.

Compressive Strength Test.—This is carried out in a similar manner to the tensile strength test, but using a suitable type of compressive strength testing machine equipped with means for ensuring true vertical loading in the form of a ball-and-socket device and with polished metal faces. The final storage phase in the case of exclusively dry-stored compression specimens should be a period of two days under fresh quicklime. Compression specimens withdrawn from wet storage are tested immediately while wet. The load is applied in the testing machine at the rate of approximately 18 lb. per sq. in. in twelve seconds.

Accelerated Qualitative Test for Hydraulicity

The following method is used by the Building Research Station: The accelerated qualitative test for hydraulicity is made on tensile strength briquettes prepared in accordance with the method given on p. 322 on specimens stored for twenty-eight days under "dry"

conditions, and then immersed in water in a metal tray in the manner detailed, each briquette being rested symmetrically on two parallel cylindrical glass rods ½ in. in diameter. Twenty-four hours after the moment of immersion of the briquettes they are carefully examined in a good light without disturbing them in any way, for signs of collapse or disintegration.

If no definite signs are detectable, the lime is reported as "Moderately Hydraulic (28-day test)": in each case the briquettes are preserved in water-storage for tensile strength tests at three months and subsequently. If signs of collapse or disintegration are observed the "combined storage" tests are discarded, and the lime reported as "Non-Hydraulic." The tray must not be disturbed after the briquettes have been submerged, nor must the water be agitated in any manner. The temperature of the water during the test is maintained between 14° and 20°.

Soundness.—This test is usually applied to hydrated lime and is omitted in the case of quicklime. The purchaser expects to use the former immediately, or, at the most, after a soaking overnight; while the soundness of the lime putty necessarily depends on the method of slaking and on the time of maturing allowed.

A pat of mortar 4 in. in diameter and ¼ in. thick, made with one part by weight of the lime to five parts by weight of standard sand and sufficient water to form a plastic mass, is allowed to set in air for 24 hours. It is then covered with a thin coat of fresh lime paste and allowed to set for another 24 hours. The pat is then subjected to the action of saturated steam for five hours, and should show no signs of pitting, cracking, or disintegration. A vessel similar to that described under the Faija Test for Portland cement (see p. 355) is admirable for the steam test.

Leighton Buzzard sand identical with that specified for use with Portland cement should be used (see p. 361).

IV.—HYDRAULIC ADMIXTURES (POZZOLANAS).

Pozzolanic materials are not in themselves cementitious but possess constituents capable of uniting with hydrated lime, in the presence of moisture, to form compounds possessing this quality to a high degree. Hence their addition to lime mortar imparts hydraulic properties, and greatly increases the ultimate strength. They were much used by the ancient Greek and Roman builders.

For some years the practice has grown, particularly on the continent, of adding pozzolanic material to Portland cement mortar. The reason for this is simple. The free slaked lime, which is present

in set Portland cement, is readily attacked by numerous chemical substances, and it is this readiness of attack which frequently leads to instability of the product. Hence the introduction of a material capable of combining with the free lime to form more stable compounds, greatly increases the resistance of the set cement to chemically destructive agencies.

Thus the use of pozzolanic material in Portland cement mortar increases the resistance of the resultant concrete to sea water. Again, Stradling and Brady[1] have shown that the use of a similar aggregate is valuable in fire resistance construction.

Pozzolanas may be classified as follows :—

(*A*) Natural Pozzolanas.
Italian Pozzolanas, Santorin Earth, Trass, Diatomaceous Earth.

(*B*) Artificial Pozzolanas.
Granulated Blastfurnace Slag, Burnt Clay.

Numerous other materials of feebly pozzolanic activity, and fairly common occurrence have not been included in the above classification. Some furnace clinkers also possess pozzolanic properties, but the behaviour of this class, as a whole, is so variable that they must be excluded.

Natural Pozzolanas

The natural pozzolanas are of volcanic origin, and the Roman builders used volcanic ash from the neighbourhood of Vesuvius, in their constructional work. The chief sources of supply are at Pozzuoli, near Naples, at Civita Vecchia and near Rome. Similar deposits occur and are worked in Auvergne (France) and in the Canary Islands. Santorin earth is found at the Greek island of Santorin. Trass is found in Germany, in the Eifel district and in Bavaria. It is much used by the continental engineers, in the form of trass-cement concrete, and has occasionally been exported to Great Britain for this purpose.

Attempts to utilise diatomaceous earth as a pozzolanic material have been made chiefly in Denmark and the United States. The Harbour Works Department of the Danish Government have admitted the use of their local material "moler," in the proportion of 27·5 per cent. of finely ground and air-dry moler, mixed with 72·5 per cent. of cement. Even so the finished concrete has shown considerable variations in strength. In the United States, the Bureau of Standards (1924) suggested that the workability of

[1] *Fire Resistant Construction*, D.S.I.R. Building Research Tech. Paper, No. 8.

Portland cement concrete was improved by the addition of a few per cent. of diatomaceous earth (celite), and it has been used for this purpose.[1]

Experiments at the Building Research Station, on the effect of adding American celite to sand lime, have shown that the material possesses marked pozzolanic action. Difficulty arises in the addition of a high proportion of celite to lime sand, or cement sand mortars, that owing to the bulkiness of the material, a large proportion of gauging water is required to produce a plastic mixture; the shrinkages during drying are correspondingly high. Apart from the use of a small proportion of diatomaceous earth in cement mixtures to improve workability, the possibility of shrinkage difficulties, and the extremely bulky, porous nature of the normal product, would appear to preclude the use of it as a major pozzolanic addition to mortars, except for special purposes where such properties are not objectionable.

Typical chemical compositions are given in the following tables:—

	Italian Pozzolana.	Santorin Earth.	Trass.
Water	Up to 12 per cent.	4·29	3-12 per cent.
Silica	52-60 ,,	65·43	49-59 ,,
Titanic oxide	...	0·69	...
Alumina	9-21 ,,	15·01	10-19 ,,
Manganous oxide	...	0·50	...
Ferric oxide	5-22 ,,	1·88	4-12 ,,
Ferrous oxide	...	2·06	...
Calcium Oxide	2-10 ,,	2·84	1-8 ,,
Magnesium oxide	Up to 2 ,,	1·06	1-7 ,,
Alkalis	3-16 ,,	7·61	5-10 ,,

Artificial Pozzolanas

Undoubtedly the most valuable artificial pozzolana at present in use is granulated blastfurnace slag. When ground and mixed with lime it generally exhibits good cementitious properties. It is used extensively as an addition to Portland cement, mixtures of certain proportions being known as Portland blastfurnace cement.

Burnt clay has been much used by the native builders in India, under the name of "surkhi," as a pozzolanic addition to lime mortar. It has also received official recognition by Anglo-Indian civil engineers. There is little doubt that many clay deposits in Great Britain would function admirably as pozzolanic materials, if lightly burnt, but their use hitherto would seem to have been more accidental than otherwise.

[1] *Engineering News Record*, 1925, p. 995.

Nature of Pozzolanic Action.

It was generally supposed that pozzolanic activity was due to the presence of "soluble silica." The proportion of ingredients soluble in hydrochloric acid is shown in the following analyses:—

	Pozzolana Italy (Rivot).	Pozzolana Auvergne (Rivot).	Trass Rhine (Elsner).
Soluble in HCl:—			
Silica	19·5	28·2	11·5
Alumina . . .	9·7	2·0	17·7
Ferric oxide . . .	6·5	21·8	11·8
Calcium oxide . .	8·0	9·0	3·2
Magnesium oxide . .	0·9	...	2·2
Alkalies	2·6	1·2	2·7
Insoluble in HCl:—			
Silica	32·7	25·0	37·4
Alumina and ferric oxide	8·1	6·7	1·8
Calcium oxide . .	1·2	1·3	2·2
Water and loss . .	10·2	4·1	9·5

Lunge and Millberg, however, came to the conclusion that easily decomposed silicates, and not free silica, were the active substances in natural pozzolanas. These contained no free amorphous silica, but did contain besides refractory silicates, presumably active silicates of the nature of zeolites.

The actual effect of the pozzolana is to combine with the lime to form insoluble silicates and aluminates. To this action is due the power that pozzolanic mixtures possess of setting under water, and in the absence of atmospheric carbon dioxide. They are, therefore, able to acquire considerable strength in damp positions, or in the centre of masses of masonry, where ordinary lime-sand mortar would never really set.

Testing of Pozzolanas

Fineness. Since reaction between the active ingredients of a pozzolana and the hydrated lime can only take place at the surface of the particles, it follows that extreme fineness of the pozzolanic addition is desirable. The degree of fineness should be determined by sieving. A satisfactory standard is that usually accepted for Portland cement, viz., a residue on a 76×76 mesh sieve not greater than 1 per cent., and a residue on a 180×180 mesh sieve not greater than 10 per cent.

Pozzolanic Activity. In view of the paucity of information available on this subject, the most reliable test is undoubtedly a practical one. A portion of the material to be tested should be mixed with half its

own weight of dry slaked lime and the mixture made into a pat of suitable consistency. The pat should be placed on a glass plate and stored in moist air, for some days or weeks according to the rate of hardening. During this time its behaviour should be noted and compared against a pat of lime putty, mixed at the same time and stored under similar conditions. Under the moist conditions prevailing the lime pat sets very slowly, and pozzolanic activity in the material under test is indicated by the more rapid hardening of the other pat.

The following test has been used at the Building Research Station.[1] A small quantity of the finely powdered material is added to rather less than its own weight of slaked lime, in a tube or small narrow bottle and covered to a depth of 2 in. with pure water. It is shaken every twelve hours for a week. The appearance of the tube shortly after shaking is observed, and sediment compared with another pozzolana similarly treated. The actual quantities recommended are 0·5 g. of the powdered pozzolana, 0·3 g. of the slaked lime, and 20 c.c. of distilled water in medium size test tubes.

The interaction between the solution of lime in water and the pozzolana gives rise to hydrated alumino-silicates of complex or indefinite structure; these hydrates will be formed in the colloidal condition, and are much more bulky than the clay or lime, with the result that after seven days the tube will contain an increased volume of solid matter as measured by the height it extends up the tube, also the rate of settlement, owing to its flocculent nature will be slower; the activity of the pozzolana can therefore be judged by inspecting the tubes at different times after shaking. In comparison, the volume of the solid matter in a similar tube immediately after mixing will be much smaller, and it will settle almost immediately.

V.—HYDRAULIC CEMENTS

A. Natural Hydraulic Cements

Hydraulic cements are distinguished as natural or artificial according as they are obtained by merely calcining a naturally occurring mineral, or by working up two or more materials.

The chief representative of the former class is Natural or Roman cement. This material is distinguished from the hydraulic limes hitherto treated, by refusing to slake and needing artificial comminution before it can be applied as cement. It finds but little commercial application in this country partly owing to the absence of naturally occurring deposits in sufficient quantity to warrant working, and

[1] *Lime and Lime Mortars*, D.S.I.R. Building Research Special Report, No. 9.

partly owing to the high grade and comparative cheapness of Portland cement. Its use is much more general on the Continent and in the United States.

The analytical examination of Natural cement is conducted exactly as for hydraulic lime (p. 309).

The following is an average analysis of Natural cement ;—

Silica	Up to 27 per cent.
Alumina	8 to 10 ,,
Ferric oxide	3 to 6 ,,
Calcium oxide	48 to 59 ,,
Magnesium oxide . . .	up to 3 ,,
Sulphuric acid	,, 2 ,,
Alkalis	,, 1 ,,

If the chemical composition of a given material lies within these limits, it is fairly certain that the article is of good quality; but its real nature can only be decided by the mechanical tests for setting, permanency of volume and strength.

In examining a raw material from which Natural cement is made, constancy of chemical composition is a criterion of quality, as the stone goes straight to the kiln; an artificial adjustment of the quality, as in the case of Portland cement, is excluded. Since Natural cement must be ground before use, the fineness of the powder should be determined, as the strength of the mortar made from it increases with the degree of fineness. Natural cement is not burnt to incipient fusion, that is, not to maximum density, and consequently the calcined product retains its looseness of texture, and the ground powder is comparatively soft and impalpable.

Natural cements may be defined as products obtained by calcining argillaceous marls below the point of incipient fusion, so that they do not slake with water and have to be powdered mechanically. The specific gravity varies between 2·7 and 3·0; it very rarely exceeds the latter. The loss on ignition is 5 per cent. or less. Its colour is yellowish to reddish-brown.

Roman cements absorb water and carbon dioxide with avidity, and must therefore be kept, before testing, in air-tight vessels, as otherwise they deteriorate in quality. As a rule they set with tolerable rapidity; incipient hardening is observed with rapid setting cements in seven minutes, with medium setting cements in fifteen minutes or less, and with slow-setting cements in upwards of fifteen minutes. The time of setting is determined as for Portland cement (p. 351).

Roman cements must permanently keep the shape in which they have hardened. A cake of cement which has been placed under water twenty-four hours after gauging or setting should show no cracks or distortions whatever after twenty-eight days' immersion.

They are sufficiently used in the United States to warrant the issue of a specification.[1] The chief points of this are as follows: Fineness: The residue on a No. 100 sieve should not exceed 10 per cent. and that on a No. 200 sieve should not exceed 30 per cent. Setting time: This is determined by means of the Vicat needle (p. 351). The initial set should not occur under ten minutes and the final set should not take place under thirty minutes, nor be prolonged above three hours.

Tensile Test. This test is carried out as for Portland cement, p. 357, and the material must attain the following minimum breaking strain:—

Neat Test—	
24 hours in moist air	75 lb. per sq. in.
7 days (1 day moist air and 6 days water)	150 „ „
28 „ (1 „ „ 27 „)	250 „ „
Mortar Test (3 parts sand, 1 part cement)—	
7 days (1 day moist air and 6 days water)	50 lb. per sq. in.
28 „ (1 „ „ 27 „)	125 „ „

The actual strength of the best sorts of Roman cement exceed these minimum figures very considerably; their breaking strains may reach 20 kg. and 180 kg. per sq. cm. (284 and 2562 lb. per sq. in.) after twenty-eight days. Secondary setting generally proceeds for a year or so, and strengths approaching 30 kg. and 300 kg. per sq. cm. (427 and 4270 lb. per sq. in.) by tension and compression respectively are then attained. The strength of unmixed Roman cement is also high compared with that of hydraulic lime; the tensile strength after seven days is 12 to 15 kg., after twenty-eight days 20 to 30 kg. per sq. cm. (171 to 213 and 284 to 427 lb. per sq. in.).

Soundness. Two pats of neat cement about 3 in. in diameter, ½ in. in thickness at the centre and tapering towards the edges, are made up in glass plates and kept in moist air for twenty-four hours. The pats are then stored as follows:—

(*a*) A pat is kept in air at normal temperatures.

(*b*) Another pat is kept in water, maintained as near as possible at 70° F.

The pats are observed at intervals up to twenty-eight days, and to pass satisfactorily the test piece should remain firm and hard and show no signs of distortion, checking, cracking, or disintegrating.

B. Artificial Hydraulic Cements. Portland Cement, etc.

Whereas all the cement materials hitherto considered are calcined and come into use in the condition of mixture in which they occur

[1] *Amer. Soc. Test Mats.*, Serial No. c. 10-09.

naturally, artificial hydraulic cements, of which Portland cement[1] is the most important, are manufactured from two or more ingredients such as limestone, marl, clay, etc.

RAW MATERIALS

Of the raw materials used in the manufacture of artificial hydraulic cements, limestone and marl have already been dealt with as regards chemical analysis (p. 294 *et seq.*).

Clay.—The materials grouped under this heading, and used for Portland cement manufacture in different parts of the country, although varying from soft London clay to hard shales or slate, are nevertheless all dealt with in a common method of chemical analysis. A slight modification is necessary when dealing with river muds. This is given on p. 335.

The sample for analysis should be dried at 110° and preserved in a weighing bottle.

Silica. About 0·5 g. of the finely powdered clay is intimately mixed with about 4 g. of fusion mixture and transferred to a platinum crucible, and the analysis carried out as described on p. 296.

Ferric Oxide and Alumina are determined as on p. 339. They are ignited in a platinum crucible and weighed as mixed oxides. The separation should be conducted by the method given on p. 4. The difference between the ferric oxide and mixed oxides is more accurately described as alumina and titanium oxide, as some clays contain appreciable amounts of the latter. As a rule its separate determination is not called for, but if required may be done as described on p. 6.

Lime is determined as on p. 340. The precipitate is ignited over a blast flame to constant weight. It is weighed as caustic lime, CaO.

Magnesium Oxide is determined as on p. 341.

Total Sulphur, Sulphuric Anhydride, Alkalis. These should be determined as for limestone (see p. 296).

Determination of Sand. In the examination of clay to be used for cement manufacture it is not only important to know the chemical condition in which silica exists but also its physical state, *i.e.* if partially present as quartz whether the grains are large or small. Pure quartz sand if sufficiently finely powdered will combine with lime at the temperature of the rotary kiln, so that it is important that the sand shall be present in fine grains.

A rough test can be made by washing 100 g. of the clay or mud on to a 180 × 180 cement sieve and continuing the washing until all the fine material has passed through the sieve and only the coarse residue remains. This residue is dried and weighed and then examined

[1] For details of the manufacture of Portland cement, see *Calcareous Cements*, Redgrave and Spackman, London, 1924. *Cements, Limes, and Plasters*, Eckel, New York, 1922.

microscopically for size and under polarised light, the latter test to give some indication of whether the residue is quartz or otherwise. A more accurate determination of the sand may be made by either of the methods given below.

(*a*) About 2 g. of the dry clay is weighed and transferred to a platinum dish. It is treated with a quantity of 1 : 1 sulphuric acid and the dish heated strongly for about ten hours, at the conclusion of which nearly the whole of the sulphuric acid should be expelled. The contents of the dish are diluted with water, heated for a short time and then washed several times by decantation, taking care that no fine sand is lost. The contents of the dish are then extracted with a strong boiling solution of sodium carbonate for a few minutes. This is allowed to settle and the supernatant solution poured through a filter. The treatment is repeated until the residue in the dish appears to reach a constant bulk. The residue is finally transferred to the filter and washed first with dilute hydrochloric acid and finally with hot water. It consists essentially of pure sand and is dried and ignited. If desired it may be further examined analytically by fusion with sodium carbonate and proceeding as for clay (p. 333).

(*b*) Fifty g. of the dried and coarsely ground sample is weighed out into capacious porcelain dish, covered with water and crude hydrochloric acid in the proportion of 3 : 1, and boiled for three hours. On cooling, the acid liquid is carefully decanted off and the residue further elutriated with water. This is most simply effected by allowing a gentle current of water to flow into the dish, whilst the solid matter is cautiously rubbed with the fingers, and the suspended clay allowed to escape by the lip of the dish until nothing but the clear sand remains behind. This simple method has the advantage of effecting a ready and complete separation of sand and clay, whereas in the ordinary elutriating apparatus the only mechanical effect which comes into play is that of the stream of water, which is often inadequate. Sometimes the clay adheres so firmly to the sand that even heating with strong sulphuric acid or boiling with caustic soda fails to free the sand entirely from clay, and the action of gently flowing water is obviously much less effective.

Combined Water and Organic Matter. For practical purposes the loss on ignition of 1 g. of material will suffice. The material should be heated strongly so that carbon dioxide, if present, is driven off. This can be determined separately and its value deducted from the total loss. Other factors, however, interfere with the true accuracy of the figure. Thus, if calcium sulphate is present, most of the sulphur trioxide will be driven off. In addition some loss of alkali will occur, and finally iron sulphide, if present, may be partially oxidised to ferric oxide and some of the sulphur volatilised.

River Muds.—Modification of the procedure given above for clay is advisable owing to the admixture of soluble salts (chlorides and sulphates, etc.) always present in river water.

About 10 g. of the dried mud is extracted with warm diluted nitric acid for a short period. The residue is collected on a paper, washed and dried at 100° and weighed. It is removed from the paper, finely powdered and preserved in a weighing bottle. Its complete analysis (including sand) is carried out exactly as for clay (p. 333).

The filtrate from the clay is made to 1 litre and examined as follows:—

Potash and Soda. 250 c.c. is taken and treated exactly as in the filtrate from the sintered mass obtained in the first stage of the method for limestone (see p. 296).

Chlorine. 200 c.c. is made faintly alkaline with sodium carbonate, a few drops of potassium chromate solution added and the chlorine estimated by titration with silver nitrate.

Silica, Alumina, Ferric Oxide, Lime, Magnesia. 250 c.c. is acidified with 15 c.c. of hydrochloric acid, evaporated to dryness on the water-bath and the procedure given under clay for these materials followed. One evaporation to dryness for silica will suffice.

Elutriation of Clay. An examination of the particle sizes of a clay or mud or an isolation of the coarse residue may also be effected by elutriation. This method consists in separating particles of different sizes or different specific gravity by suspending them in a liquid such as water which is flowing at such a velocity that it carries the smaller or lighter particles while the larger or denser ones settle to the bottom of the elutriating apparatus.

A convenient form of apparatus is Schone's elutriator. This is illustrated in Fig. 53. It consists of a tapering glass vessel about 60 cm. high, the upper portion B to C being in the form of a cylinder of about 5 cm. internal diameter. The lower portion C to D tapers from 5 cm. to 5 mm. and the lower end is connected with tube G, also 5 mm. bore. Through this tube the water or other elutriating liquid is introduced, and flows upwards through the apparatus. The narrow portion at the lower end of the vessel is necessary to ensure a truly central flow free from eddies and side currents. The top of the elutriator is constructed so as to hold a rubber stopper carrying the overflow A, which is connected to a piezometer tube 100 cm. in length, and having a small circular hole K at the apex of the downward bend.

Fig. 53.

The mud having been placed in the funnel, a stream of water from the feed tube G is made to traverse the funnel from below upwards. The advantage of the apparatus is that having once been calibrated,

the rate of flow, as represented by the pressure at the exits, can be accurately read off in the graduated tube. The elutriation can therefore be carried out at a definite and uniform pressure. When the clayey matter has been completely separated from the sand by this method, the latter is washed into a small porcelain dish and dried, first on the water-bath and then in the oven.

In order to determine the degree of fineness of the sand, either the dried sand may be sieved or, using Schone's apparatus, the sandy residue is elutriated at gradually increasing pressures and the several products determined separately. It is customary to distinguish the following grades:—

Silt: diameter of grain up to 0·025 mm.
Dust: diameter of grain up to 0·040 mm.
Fine sand: diameter of grain up to 0·200 mm.
Coarse sand: diameter of grain above 0·200 mm.

Other methods of elutriation are described on pp. 39-45 and 590.

PORTLAND CEMENT

Composition of Portland Cement

In the United States Government Specification for Portland Cement,[1] the following definition is to be found: "Portland cement is the product obtained by finely pulverising clinker produced by calcining, to incipient fusion, an intimate and properly proportioned mixture of argillaceous and calcareous materials, with no additions subsequent to calcination excepting water and calcined or uncalcined gypsum." A similar definition is also to be found in the specifications drawn up by the British Engineering Standards Association.[2] The clause thus cited is intended to define clearly the method of manufacture, and to exclude the so-called "Natural" cements, which are calcined without previous grinding or mechanical mixing. It does not take cognisance of the proportions in which the various constituents should be present, and for this purpose numerous formulæ have been devised.

The chemical composition of a good Portland cement is generally found to be within the following limits:-

	Per cent.
Silica	18 to 26
Alumina	3 „ 10
Ferric oxide	2 „ 5
Calcium oxide	57 „ 66
Magnesium oxide	0·5 „ 3
Sulphuric anhydride	0·5 „ 2·5
Water and carbon dioxide	1 „ 3

[1] "United States Government Master Specification for Portland Cement," Circular of the Bureau of Standards, No. 33 (4th ed., April 1927).

[2] British Standard Specification for Portland Cement, B.E.S.A. (1925).

An increase in the proportion of lime invariably yields a stronger cement, until a maximum limit is exceeded, when the product becomes unsound. An increase in the alumina hastens the setting and the difference between slow setting and quick setting cements, other factors being equal, is mainly dependent on this characteristic. Ferric oxide functions similarly to alumina, and in calculating the proportions of a mixture the sum of these two components is always taken. Owing to the lower melting point of ferrites, as compared with aluminates, the substitution of ferric oxide for alumina lowers the sintering point of the material. Alkalis also behave in a like manner. In considering the formulæ below it must be stressed that hitherto the chemical compounds which go to form Portland cement have been but dimly comprehended, and that these formulæ derive their value rather from practical observation than from theoretical reasoning.

Lime Ratio. This is the formula favoured by the British Engineering Standards Association. It expresses the proportion (*in chemical equivalents*) between the lime on one hand and the silica and alumina on the other. Before making the calculation the proportion of lime necessary to combine with the sulphuric anhydride must be deducted from the total lime present.

$$\text{Lime ratio} = \frac{CaO}{SiO_2 + Al_2O_3}.$$

In general practice the value for a good cement is between 2·4 and 2·8. The specification allows a somewhat wider limit, the minimum value being 2·0 and the maximum value 2·85.

Silica Ratio. This formula expresses the actual proportion (*not chemical equivalents*) between the percentage of silica and the combined percentage of iron oxide and alumina.

$$\text{Silica ratio} = \frac{\text{Percentage of silica}}{\text{Percentage of alumina} + \text{percentage of iron oxide}}.$$

As a general rule the silica ratio is about 2·5 although exceptions are comparatively frequent. A high silica ratio, *i.e.* above 2·7, is generally associated with a slow hardening cement, but care must be exercised by the manufacturer, otherwise unsound products are easily produced, due to incomplete combination between the lime and silica. A low silica ratio is generally associated with a quick hardening cement which develops its strength at an early date.

Hydraulic Index. This formula represents the ratio between the acid elements, silica and alumina, and the basic elements, lime and magnesia, viz.,

$$\text{Hydraulic index} = \frac{\text{Silica} + \text{alumina}}{\text{Lime} + \text{magnesia}}.$$

As a general rule the commercial cements have a value between 0·42 and 0·48. This ratio is but little used in Great Britain, but finds more favour in France. In the French Standard Specification for Portland cement for works to be executed in sea water the hydraulic index must be at least 0·47 for a proportion of 8 per cent. of alumina, with a diminution of 0·02 for each 1 per cent. of alumina below 8 per cent.

Hydraulic Modulus. This formula is practically the reverse of the hydraulic index, and expresses the relation between the basic constituent, lime, and the acid constituents, silica, alumina and iron oxide. Thus:—

$$\text{Hydraulic modulus} = \frac{\text{Percentage of lime}}{\text{Percentage of silica} + \text{percentage of alumina} + \text{percentage of iron oxide.}}$$

As a general rule a good cement is found between the limits of 1·8 and 2·2. It is held that a hydraulic modulus of over 2·4 is accompanied by expansion and cracking.

Other Specified Limits. In addition to the clause cited above from the British Engineering Standards Specification, certain limits have been defined for a number of constituents. Thus the insoluble residue shall not exceed 1·5 per cent.; magnesia shall not exceed 3 per cent.; and the total sulphur calculated as sulphuric anhydride (SO_3) shall not exceed 2·75 per cent. The total loss on ignition shall not exceed 3 per cent.

Somewhat different limits are allowed in the specifications of the United States, these being:—

	Per cent.
Loss on ignition	4·00
Insoluble residue	0·85
Sulphuric anhydride	2·00
Magnesia	5·00

Sampling.—When sampling large quantities of cement for analysis or testing, it is advisable to take a series of small samples from a variety of points in the heap or store. The method of a single sample taken at random from only one place in a store or from one sack of a consignment should not be adopted. The small samples should not be taken entirely from the surface of the material, where the cement may vary somewhat from that of the interior by reason of atmospheric influences. Samples from the interior of a bulk may be conveniently obtained by using a long iron tube sharpened at one end and carrying inside a removable stick. To take a sample the tube should be forced deeply into the pile and the stick withdrawn. The tube is then forced a little deeper into the cement, and when withdrawn the required material will be found at the end of the tube. The samples of cement thus obtained should be mixed together by turning over with a trowel.

The following clause governing the sampling of cement is included in the British Standard Specifications. "A sample or samples for testing may be taken by the purchaser or his representative, or by any person appointed to superintend the works for the purpose of which the cement is required or his representative, or by any expert analyst employed or instructed by such purchaser or person, or the representative of such purchaser or person. Each sample for testing shall consist of approximately equal portions selected from twelve different positions in the heap or heaps when the cement is loose or from twelve different bags, barrels or other packages when the cement is not loose, or where there is a less number than twelve different bags, barrels or other packages, then from each bag, barrel or other package. Every care shall be taken in the selection, so that a fair average sample may be taken."

CHEMICAL ANALYSIS

Silica. 0·5 g. of the cement is weighed out and transferred to a platinum or porcelain dish. The weighed portion is triturated with a few c.c. of water, and 10 c.c. of concentrated hydrochloric acid added. The dish is transferred to a water-bath, the contents evaporated to dryness and then heated on a sand-bath for one hour at about 150°. When cool 10 c.c. of 1 : 1 hydrochloric acid is added, and the dish placed in a warm place for ten minutes. The contents are filtered and the silica washed with warm water until free from chlorides. The filtrate is again evaporated to dryness and treated exactly as in the first instance, the silica being collected and washed on a separate filter. The two precipitates are combined in a platinum crucible and ignited in the muffle, and finally over the blast flame to constant weight. The increase in weight represents the silica plus a small quantity of insoluble matter. A separate determination of the insoluble matter is made (see below) and its weight deducted from the combined weight obtained above to arrive at the true silica content.

Two evaporations to dryness are necessary to separate the silica completely. Blount claims that it is possible to obtain a complete separation of the silica by one evaporation only, providing the substance is evaporated to dryness in an extremely thin layer in the dish. The evidence of many other experimenters, however, fails to support this contention, and it is not to be recommended; the method sometimes suggested of making two evaporations to dryness without an intervening filtration, fails to give a complete separation and should not be adopted.

Oxides of Iron and Aluminium. The filtrate and washings from the silica are warmed and a few drops of nitric acid or bromine water added. A slight excess of ammonium hydroxide is added, and the

contents of the beaker brought to boiling and filtered immediately. The solution filters rapidly and there is nothing to be gained by allowing the precipitate to settle and washing by decantation. The precipitate is washed three times with hot water, and the filtrate and washings caught in a large beaker and set aside. The precipitate is dissolved in hydrochloric acid and reprecipitated as above. It is again filtered and washed well with warm water containing ammonium nitrate (20 c.c. of nitric acid is neutralised with ammonium hydroxide and added to 1 litre of water). The precipitate is ignited and weighed as mixed oxides. In washing the above precipitate the precautions noted under the determination of mixed oxides in limestone (see p. 296) should also be borne in mind.

Separation of Iron Oxide and Alumina. This may be most conveniently carried out by making a separate determination of the iron oxide by the dichromate method, and arriving at the alumina by difference between this figure and the figure of the mixed oxides. 0·5 g. of cement is triturated in a 400 c.c. beaker with a little water and 10 c.c. of hydrochloric acid added. It is warmed until solution is complete. The iron is reduced to the ferrous state by the addition of stannous chloride drop by drop. The reduction is complete when the solution becomes colourless. The contents of the beaker are diluted to about 200 c.c. with cold water, 10 c.c. of a saturated solution of mercuric chloride added, and the solution then titrated with potassium dichromate using potassium ferricyanide as a spot indicator. For strength of solutions see p. 176.

Calcium Oxide. The two filtrates from the mixed oxides of iron and aluminium are combined, 10 c.c. of ammonium hydroxide added, the solution brought to boiling, 20 c.c. of a saturated solution of ammonium oxalate slowly added, and the boiling continued until a granular precipitate is formed. The beaker is removed to a cool place for one hour, when the contents are filtered and the precipitate washed three times by decantation with warm water. Any precipitate on the paper is rinsed into the beaker and the whole precipitate dissolved in a hydrochloric acid. The calcium oxalate is precipitated as before. After standing it is filtered through the previous filter and washed well with warm water. The washed precipitate is dried and then ignited over a blast flame to constant weight. It is weighed as caustic lime, CaO.

To separate calcium from magnesium, at least two precipitations are necessary. Furthermore they are imperative when sodium carbonate has been incorporated in the original ignition of the sample, the tendency of calcium oxalate to absorb sodium salts being well recognised. Too long washing of the final precipitate is also avoided. This is desirable owing to the appreciable solubility of calcium oxalate in

hot water. Hildebrand[1] states that a litre of nearly boiling water will dissolve over 1 centigram of this precipitate. At room temperatures 7 mgm. are dissolved.

Magnesium Oxide. The filtrates from the two lime precipitations are combined, evaporated to 250 c.c. and cooled. Five c.c. of a 10 per cent. solution of sodium phosphate is added, and then an appreciable excess of ammonium hydroxide. The contents of the beaker are well stirred. The precipitate is allowed to settle for twelve hours. It is filtered and washed three times with ammonia water, and then returned to the precipitation beaker and dissolved in a little hydrochloric acid. The bulk is diluted somewhat, and the magnesia reprecipitated as above. The precipitate settles rapidly the second time and is usually filtered after two to three hours. It is well washed with ammonia water, dried and ignited finally over the blast flame. It is weighed as magnesium pyrophosphate, $Mg_2P_2O_7$ containing 36·2 per cent. of magnesium oxide.

Determination of Ferrous Iron. This is sometimes present in a cement in very small quantity. To estimate it, 5 g. of sample is triturated in a small beaker with an excess of water and a little sodium bicarbonate added. The mixture is washed into a flask fitted with a double bored cork, through one hole of which passes a funnel fitted with a stopcock, and through the other a tube fitted with a bunsen valve. Dilute hydrochloric acid is admitted to the flask through the funnel and the cement decomposed by heating. The ferrous iron is determined by titration with standard potassium dichromate.

Insoluble Matter. Almost all cements contain a small proportion of inert matter which is valueless as a cementitious material. In the analytical procedure it is unaffected by hydrochloric acid and is therefore found associated with the silica. It can be further differentiated from the "active" silica by its resistance to a boiling solution of sodium carbonate. It is referred to as insoluble matter, and in cements of good quality rarely exceeds 0·5 per cent. To estimate it, 2 g. of cement is stirred up in 100 to 150 c.c. of water in a beaker, 10 c.c. of hydrochloric acid added, and the contents boiled for a few minutes. Solution is almost immediate, and prolonged digestion is undesirable owing to a tendency for gelatinous silica to separate out. The insoluble portion is collected on a filter and washed free from acid. It is returned to the beaker and digested for fifteen minutes with a boiling solution of sodium carbonate. The mixture is filtered hot, through the paper used for the acid filtration. It is washed free from sodium carbonate with hot water, ignited and weighed.

Loss on Ignition. One g. is heated to a low cherry-red heat in a platinum crucible to a constant weight. The loss is generally inferred

[1] *op. cit.*, p. 141.

to be carbon dioxide and water. Hence, an extreme temperature should be avoided, as it involves risk of loss by volatilisation of sulphuric acid.

Sulphuric Anhydride. 0·5 g. of cement is triturated with a little water in a dish and dissolved in 10 c.c. of hydrochloric acid. The solution is evaporated to dryness, the dried mass redissolved in dilute hydrochloric acid and the silica removed by filtration and washed with hot water. The bulk of filtrate should be about 150 to 200 c.c. To this 10 to 15 c.c. of a 10 per cent. solution of barium chloride is added and the whole allowed to stand for several hours. The barium sulphate is filtered off, well washed with hot water and weighed. It contains 34·3 per cent. of sulphuric anhydride.

The evaporation to dryness and subsequent filtration is intended to remove the main portion of the silica, which would otherwise tend to contaminate the barium sulphate.

Determination of Sulphide Sulphur. Sulphur is occasionally found in Portland cement as calcium sulphide.

The determination is carried out as follows: Five g. is mixed with water to form a thin paste and rinsed into a flask fitted with a two-holed rubber cork through which pass the stem of a tap funnel and a tube bent twice at right angles to lead the evolved gases to the bottom of a tall cylinder containing a solution of cadmium chloride. Dilute hydrochloric acid is introduced into the flask through a stoppered funnel and the flask heated until the contents have boiled for a few minutes, after which the delivery tube is quickly withdrawn from the cylinder. If this precaution is not taken, the cadmium chloride solution is sucked back into the flask on cooling. The contents of the cylinder are washed into a 500 c.c. beaker, thoroughly cooled and diluted to 300 c.c. with cold water. Hydrochloric acid is added to make the solution acid and 10 to 15 c.c. in excess. One c.c. of starch solution is added, and the solution titrated immediately with iodine solution until a deep blue colour is obtained, which does not disappear on standing two or three minutes. The solutions are prepared as follows:—

Starch Solution. A few g. of soluble starch are mixed into a thin slip with cold water and poured into 400 c.c. of boiling water. When cool the solution is ready for use.

Iodine Solution. 3·96 g. of iodine and 6 g. of potassium iodine are dissolved in water and made to 1 litre. One c.c. of this solution should be equivalent to 0·0005 g. of sulphur. If 5 g. of sample is taken for the analysis, each c.c. of iodine solution required = 0·01 per cent. of sulphur.

Cadmium Solution. Four g. of cadmium chloride is dissolved in 100 c.c. of water, and an equal bulk of ammonium hydroxide added.

For each estimation 5 c.c. of this stock solution and 15 c.c. ammonium hydroxide are mixed together and diluted to 60 c.c. with water.

For details of other methods, see Vol. II., p. 57 *et seq.*

Alkalis. These are determined as described on p. 9.

Rapid Estimation of Lime. Either of the rapid methods given for limestone may be adopted. About 0·3 g. of the material is dissolved directly in hydrochloric acid and a few drops of nitric acid. The latter is added in order to oxidise any ferrous iron or calcium sulphide which might be present, and which would otherwise reduce the permanganate and give high results.

Rapid Estimation of Magnesium. Since a high percentage of magnesia throws a suspicion of unsoundness upon a Portland cement, a separate estimation of magnesia is sometimes desirable. The following procedure may then be adopted. Two g. of the cement is decomposed in a capacious porcelain dish, the solution diluted with water, heated to boiling, and the aluminium, iron and calcium precipitated, together with part of the silica, by ammonia and ammonium oxalate. The liquid, including the suspended matter, is washed into a litre flask, cooled, made up to the mark and thoroughly shaken. After settling, 400 c.c. of the clear solution is filtered off into a beaker, about 80 c.c. of ammonia added and the magnesia precipitated as usual with sodium phosphate. The whole operation takes from two to three hours. After allowing to stand overnight the magnesium precipitate is filtered off and ignited ; the results are correct within 0·25 per cent. This method requires only twenty-four hours from start to finish, and is well adapted to the simultaneous testing of several samples.

EXAMINATION OF THE PHYSICAL PROPERTIES OF PORTLAND CEMENT

Specific Gravity.—Great attention was at one time paid to this test, but in recent years it has been realised that many of the arguments quoted in its favour are fallacious, hence its gradual elimination from many specifications. Its original value was based on the assumption that an abnormally low specific gravity arose from underburning, or the introduction of adulterants. The former point has been refuted by many workers, among whom may be cited, as an example, Redgrave and Spackman,[1] whose experimental results clearly dispute this view. Again, the value of the test as indicating the introduction of adulterants was greatly overrated, for while it would be possible to detect a large admixture of any light adulterant, other foreign materials such as slag could be mixed with the cement in large quantities without lowering the specific gravity below the limits

[1] *Calcareous Cements*, 1924, p. 105.

usually prescribed in specifications. Lastly, it has been shown by Butler[1] that a low specific gravity may be caused by aeration of the material, and as this in itself is generally advantageous the test becomes unnecessarily severe.

Provided the test is intended as the preliminary step to a logical investigation of the material, it may be regarded as useful, but otherwise too much attention should not be attached to the results. Thus if a low specific gravity is indicated it should be ascertained by a redetermination on an ignited portion of the sample, and by a moisture determination, how much of it is due to ageing. If this proves to be the entire cause, there is no reason for rejecting the material providing the strength tests are satisfactory. If on the other hand a low value is not due to ageing alone, the material should be examined for adulteration, and if this test is negative it may be due to pronounced underburning. Only in this manner can the test be made useful.

The specific gravity can be determined in the usual way by means of the specific gravity bottle, a liquid without action on cement being substituted for water. Either paraffin or turpentine is generally employed; whichever liquid is used must be absolutely free from water. This may be ensured by allowing it to stand over freshly burnt quicklime some time before use. If the specific gravity bottle is used, the specific gravity of the liquid must also be known. This should be determined with the specific gravity bottle and not with a hydrometer. The determination of the specific gravity of a fine powder is an operation demanding considerable care and some skill, on account of the tenacious retention of air by the powder. In so finely divided a product as a well-ground cement each particle is surrounded by a layer of adhering air, and this air is not dislodged at once when the particle is immersed in a liquid. Only by careful shaking and tapping can the air be made to collect in the form of bubbles, and rise to the surface of the liquid.

The method of determining the specific gravity by means of the specific gravity bottle leaves nothing to be desired as regards accuracy; but is not generally employed, as several forms of apparatus have been devised in which the volume of liquid displaced by a known weight of cement is directly read off, and the specific gravity calculated by dividing the weight of cement taken by the volume of liquid displaced. This method permits of a speedier determination and is well suited where a number of tests are to be made.

Blount's Volumemeter. This apparatus is illustrated in Fig. 54. It is extremely simple, and is capable of giving good results. It consists of a flask with a broad, flat bottom, having a capacity of exactly 64 c.c. up to the lowest graduation. Above this graduation the neck is divided into tenths. The first graduation is marked 14 and the

[1] *Proc. Inst. Civil Eng.*, 1906.

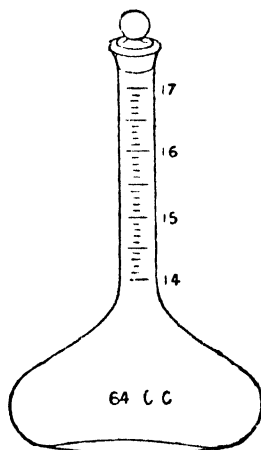
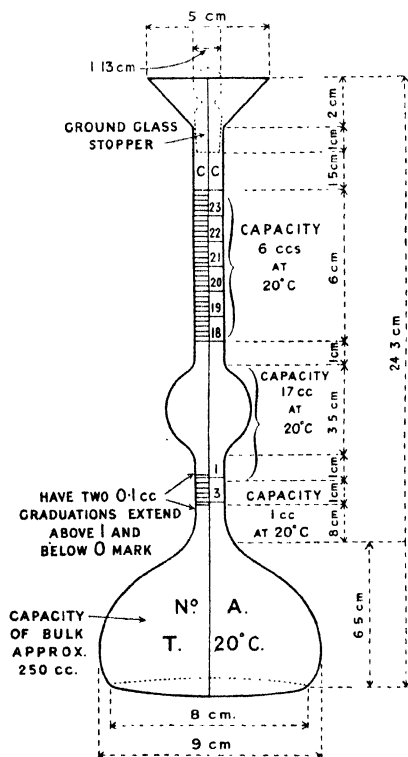
neck reads from 14 to 17 c.c. In making a determination, 50 c.c. of dry paraffin or turpentine is introduced into the flask by means of a pipette, so as to avoid wetting the neck. Fifty g. of cement is then introduced through a funnel, the flask shaken and tapped to expel the air, and the level of the liquid meniscus then read off. The volume of liquid displaced is equal to the volume of the cement. All ordinary Portland cements give a reading between 14 and 17 c.c. The specific gravity is obtained by dividing 50 (*i.e.* weight of cement) by the reading obtained. Thus if the reading is 15·9 c.c., the specific gravity is 50÷15·9=3·15.

Fig. 54.

The practice of introducing the cement into the liquid is always adopted, as it greatly expedites the removal of the adhering layer of air from the particles.

Le Chatelier Volumemeter. The slightly modified form of this apparatus, which is illustrated in Fig. 55, is that which has been adopted in the specifications drawn up by the American Society for testing materials. The flask is filled with kerosene free from water, or with benzine not lighter than 62° Baumé, to a point on the stem between zero and 1 c.c. Sixty-four g. of cement, at the same temperature as the liquid, is slowly introduced, care being taken to avoid the cement adhering to the sides of the flask above the liquid. The liquid is freed from air bubbles by tapping and rolling the flask in an inclined position. After all the cement is introduced the level of the liquid will have risen to some division of the graduated neck; the difference between this and the original reading is the volume displaced by 64 g. of cement. The specific gravity then equals the weight of cement divided by the displaced volume.

Fig. 55.

The specification cited above states that the specific gravity of the cement,

thoroughly dried at 100°, shall be not less than 3·10. The following remarks are also included. "Specific gravity is useful in detecting adulteration or underburning. The result of tests of specific gravity are not necessarily conclusive as an indication of the quality of the cement, but in combination with the results of other tests may afford valuable indications."

Fineness.—The degree of fineness of Portland cement is of considerable importance. In the first place a fine powder is able to coat the surface of an aggregate more completely than a coarse one, hence producing a more efficient mortar. In the second place the phenomenon of setting, which is the result of interaction occurring at the surface of particles with the surrounding water, is favoured by the increase in surface in proportion to mass resulting from fine grinding. Hence the effect of fine grinding is to increase the rapidity of setting, and in the early stages also the hardening, as compared with cement more coarsely ground. Of recent years this factor has been used in the production of certain brands of rapid hardening cements. Lastly, the soundness of cement may be improved by fine grinding, owing to the fact that the water used in gauging at once attacks any uncombined lime, and thus renders ultimate disintegration practically impossible. This point is of more interest to the manufacturer than the user, as it enables the material to withstand the hot test for soundness more easily.

It must be emphasised, however, that fineness alone is not sufficient indication of the quality of a cement. Underburnt or aluminous material is more easily ground than well-burnt clinker and readily yields a fine product. Nevertheless a cement which is shown by other tests to be of good quality is greatly increased in value by fine grinding, and for this reason the test is one of importance and should never be omitted.

The usual method of testing the fineness is by means of sieves of definite mesh per unit area.

In Great Britain the specifications of the British Engineering Standards Association are usually accepted. The sieves specified contain 5776 (76 × 76) meshes per square inch, and 32,400 (180 × 180) meshes per square inch, respectively. The mesh aperture of the coarser sieve is 0·0088 in. and that of the finer sieve 0·0038 in. After sifting continuously for fifteen minutes with the 32,400 mesh sieve the residue left on the sieve should not exceed 10 per cent. This residue is transferred to the 5776 mesh sieve and sifted for five minutes, when the residue remaining should not exceed 1 per cent. One hundred g. of cement should be taken for the test. The authors have tested many mechanical methods for agitating sieves for these tests, but have yet to observe a method which compares favourably with hand sieving.

The specifications for fineness required by authoritative bodies in various countries are shown in the following table:—

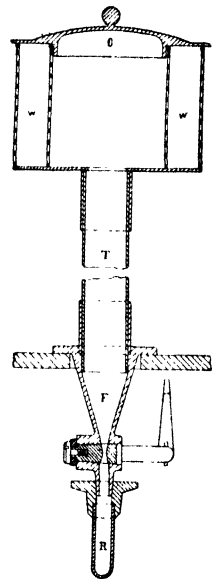
	Mesh Aperture.	Allowable Limit.	Mesh Aperture.	Allowable Limit.
Great Britain . .	0·0088 in.	1 per cent.	0·0038 in.	10 per cent.
United States . .	...	...	0·0029 ,,	22 ,,
Germany . .	0·00874 in.	5 per cent.	...	...
France	0·0137 ,,	2 ,,	0·0037 in.	40 per cent.

Comparisons from the table are somewhat difficult owing to the different mesh apertures adopted, but nevertheless a fairly common standard is indicated.

Fig. 56.

The method of determining the fineness of Portland cement by sieving has been subjected to much criticism and inquiry, chiefly on account of variations in the thickness of the wire used in the manufacture of the sieves. Although strictly precise results are not obtainable, the method may be considered sufficiently accurate for the purpose, providing reasonable care is exercised to examine each sieve microscopically before it is taken into general use.

The sieving test is limited in its application by the instrument employed, as with even the smallest mesh sieve obtainable, only the small proportion of comparatively large and inert particles which remain on the sieve is isolated. For the further subdivision of the material passing through the sieve, and for the determination of the extremely finely ground portion usually referred to as flour, other methods are used. The procedure usually adopted is separation in a current of air.

A convenient form of apparatus based on this principle is the Griffin-Goreham flourometer, the general arrangement of which is shown in Figs. 56 and 57. The supply of air as well as the pressure is regulated by a small gasholder which contains sufficient air for one test; the pressure of the air supply is indicated by a small pressure gauge. The duration of the test is about ten minutes. The air supply passes from the gasholder to the bottom of the conical receptacle F, Fig. 56, into which 10 g. of the cement to be tested has previously been placed. The finer particles of cement, the so-called "flour," are carried away up the tube T, while the coarser grains fall into the receptacle R on the cessation of the air pressure, and are then weighed. Should

the test be carried out in the open, the tube T communicates direct with the atmosphere into which the dust escapes, but if the test is made in the laboratory a covered cap is used. This consists of two concentric cylinders of perforated zinc between which cotton wadding, W, is loosely packed. The dust filter should be cleaned from time to time so as to prevent any diminution of the force of the air current.

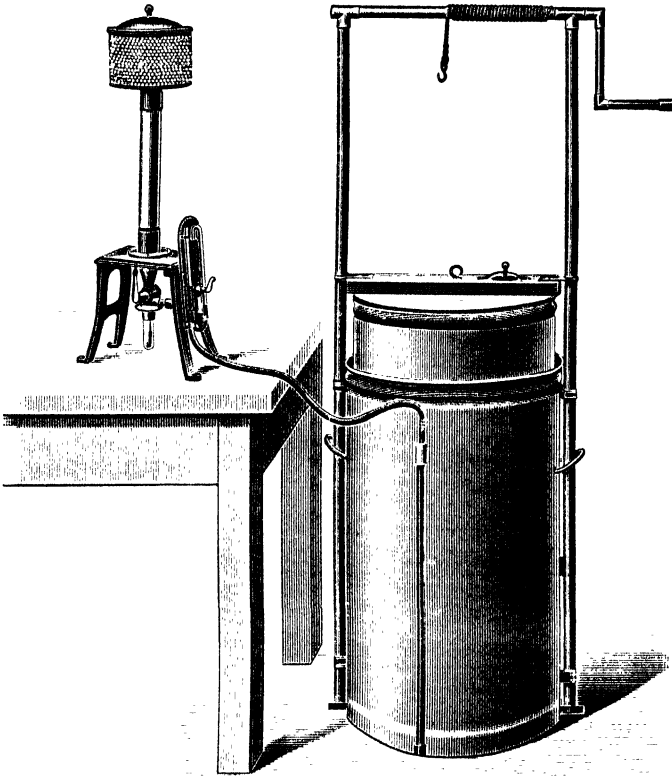



FIG. 57.

The apparatus can be standardised either by means of sieves or by an actual microscopic measurement of the coarser particles.

The following type of air elutriator has been much used by the authors and always found to give excellent results. Fig. 58 shows the general arrangement. A is a single stage, water-jacketed, axial type, belt-driven air compressor (by Reavel & Co., Ipswich); the piston displacement is 0·1 cu. ft. per min. when running at a maximum speed of 750 R.P.M. and working at a maximum pressure of 60 lb. per sq. in. This compressor delivers the air into a sheet iron air reservoir, B,

1 ft. 6 in. in diameter by 3 ft. 4 in. high. In order to destroy pulsations, this air reservoir is connected to a precisely similar one, C, by means of a 3-in. pipe. A water tank, H (7 ft. high by 18 in. wide), enables a constant air pressure to be maintained by keeping a constant depth of water in the tank and allowing the air to bubble at as steady a rate as possible. By means of the regulating valve, K, and by varying the height of water in the tank, H, one can obtain an air blast of any required constant pressure (limited by the height of water that the tank will hold) which is read on the water manometer, L, fixed vertically in front of a scale. The gas meter, D, gives the volume velocity of the air stream. This meter (by Parkinson & Cowan, Birmingham) is of the wet type, capacity 360 cu. ft. per hour, and guaranteed accurate to 0·5 per cent.; pressure limits were 10 in. to 80 in. water-gauge.

In elutriating very fine dust, much adhered to the walls of the elutriating tube, M, unless the entering air was thoroughly dried by

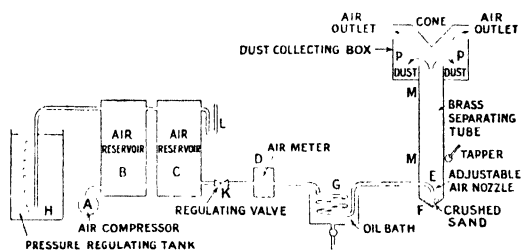



Fig. 58.

slightly warming before entering the elutriating tube. This is most easily effected by passing air after emerging from the meter, D, through a copper spiral immersed in an oil-bath, the temperature being regulated by means of a gas burner. The temperature of the entering air can thus be maintained constant, no matter what the temperature of the external air. The temperature of the air in the elutriating tube, M, is periodically taken by means of a thermometer, so that temperature corrections can be made for calculating the linear velocity of the air stream in the tube; the pressure in the tube is taken as atmospheric. After passing the warming coil, G, the air enters the elutriating tube, M, which is a considerably altered form of that described[1] by J. C. Pearson and W. H. Sligh. The air enters the elutriator tube, M, by means of a nozzle, E, fitted gas-tight into the vertical axis of the tube; the nozzle, which fits into the elutriator tube by means of a screwed collar, can easily be removed and replaced by one of a different bore.

[1] *Bur. Stand. Tech. Paper* No. 48, 1915, "An Air Analyser for Determining the Fineness of Cement," p. 25.

In order to obtain varying speeds of air, the following combinations of elutriator tubes and nozzles may be used:—

(1) 6 ft. long brass elutriator tube, 6 in. bore fitted with (i) $\frac{1}{4}$ in.; (ii) $\frac{3}{8}$ in. bore nozzles.

(2) 6 ft. long copper elutriator tube, 4 in. bore fitted with $\frac{3}{8}$ in. bore nozzle.

(3) 5 ft. long brass elutriator tube, $2\frac{3}{4}$ in. bore, fitted with (i) $\frac{3}{16}$ in.; (ii) $\frac{1}{4}$ in.; (iii) $\frac{5}{16}$ in.; (iv) $\frac{7}{16}$ in. bore nozzles.

(4) 5 ft. long brass elutriator tube, 2 in. bore fitted with (i) $\frac{1}{4}$ in.; (ii) $\frac{5}{16}$ in.; (iii) $\frac{7}{16}$ in. bore nozzles.

In order to prevent dust adhering to the walls, the elutriator tube, M, was kept in vibration by means of an iron tapper, which was

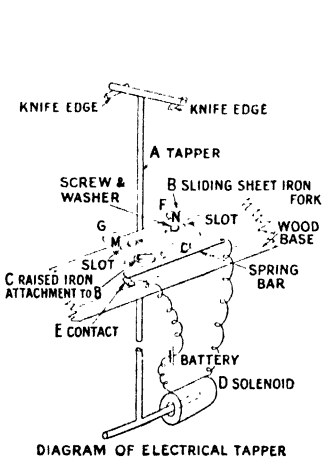
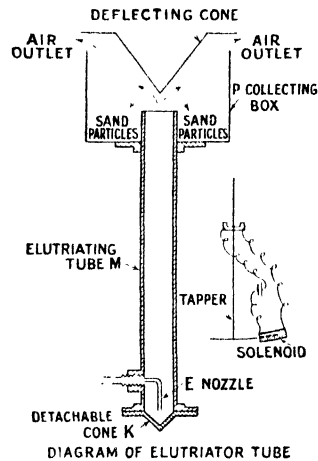



Fig. 59. Fig. 60.

controlled by a solenoid and a make-and-break contact as shown in Fig. 59. The iron tapper, A, is free to swing on two knife edges which are fixed on the elutriator staging. A solenoid, D, is fixed in such a position that the hammer of the tapper between the two prongs of a sliding iron fork, B, produces a make-and-break in an electric circuit whereby the solenoid, D, becomes alternately magnetic and non-magnetic and thus maintains the oscillations of the iron tapper, A. The method of make-and-break is as follows:—The iron tapper bar, A, swinging between the prongs, F and G, of the sliding sheet iron fork, B, strikes each prong alternately at the end of its stroke and so causes the iron sliding sheet, B, to move backwards and forwards on a wooden base, its motion being confined by two slots, M and N, clamped loosely to the board by a screw and washer, as indicated in the diagram. Attached to this sliding iron sheet, B, is a raised iron attachment, C, which, coming into contact with the spring bar, C^1, raises it, and so breaks an electrical contact at E, and thus destroys the circuit. The

solenoid, D, then ceases to attract the iron bar, which falls back by gravity and swings until it strikes the elutriator tube. In its swing the bar strikes the prong, G, slides the iron sheet, B, to the left and the iron attachment, C, is forced away from the spring bar, C^1. Electrical contact is again established at E, the solenoid, D, then again attracts the iron tapper, and the action proceeds indefinitely.

The elutriating tube is fitted at the base with cones made of cast brass ¼ in. thick, as thinner cones rapidly wear away under the abrasion of the moving particles in an air-blast. These cones, K, are bolted on to the base of the tube, M, as shown in Fig. 60, so that they could be rapidly removed and replaced. If we place cement in K, then the air entering by the nozzle, E, impinges on it and carries particles up the elutriator tube. The cement carried up the elutriator tube, M, is collected in a transparent cylindrical celluloid box, P, with a separate celluloid base and open at the top; it is composed of two half cylinders which can be easily joined together or separated by means of two brass strips fitted with screws. The separate celluloid base in turn rests on the iron base which is fixed on the tube, M. The removal of an elutriated sample and the replacement of the receiver can thus be effected easily.

Determination of the Setting Time.—It is important that the cement user should be aware of the time of setting of the cement he employs, in order that he may regulate the preliminary mixing of the aggregate. It is necessary, with quick setting materials, to complete the wet mixing of the aggregate and cement before the setting action commences, otherwise this action is seriously interfered with, and may even be retarded for several days.

Two distinct setting time tests are at present recognised, one for the commencement of the setting, called the initial set, and the other for the end known as the final set. The former test is easy to recognise and is the more valuable to the user, since it fixes the period within which the mixing of the plaster must be completed. The latter test is somewhat arbitrary and represents the period at which the surface of the test pat has hardened sufficiently to support a weighted needle.

The instrument generally employed for the determination of the rate of setting is known as the Vicat needle. This is illustrated in Fig. 61. It consists of a frame, D, carrying a movable rod, B, with the cap, A, at one end, and a removable needle, C, at the other. The needle is 1 mm. square in section and has a flat end. The rod, B, carries an indicator which moves over the graduated scale, attached to the frame. The rod, cap, and needle, etc., together weigh 300 g. The cement to be tested is held in the mould, E, which consists of a split ring resting in a non-porous plate.

Initial Set. To make a test the mould is first filled with cement gauged to a plastic condition. This is placed under the needle, which

is lowered to the surface of the cement pat. It is quickly released and allowed to penetrate the pat. The procedure is repeated at intervals, and the time noted when the needle fails to pierce the pat completely. The period elapsing between first adding the water and the point noted above is referred to as the Initial Setting Time.

Final Set. The needle D is replaced by the needle H and the periodic tests continued. The cement is considered set when the

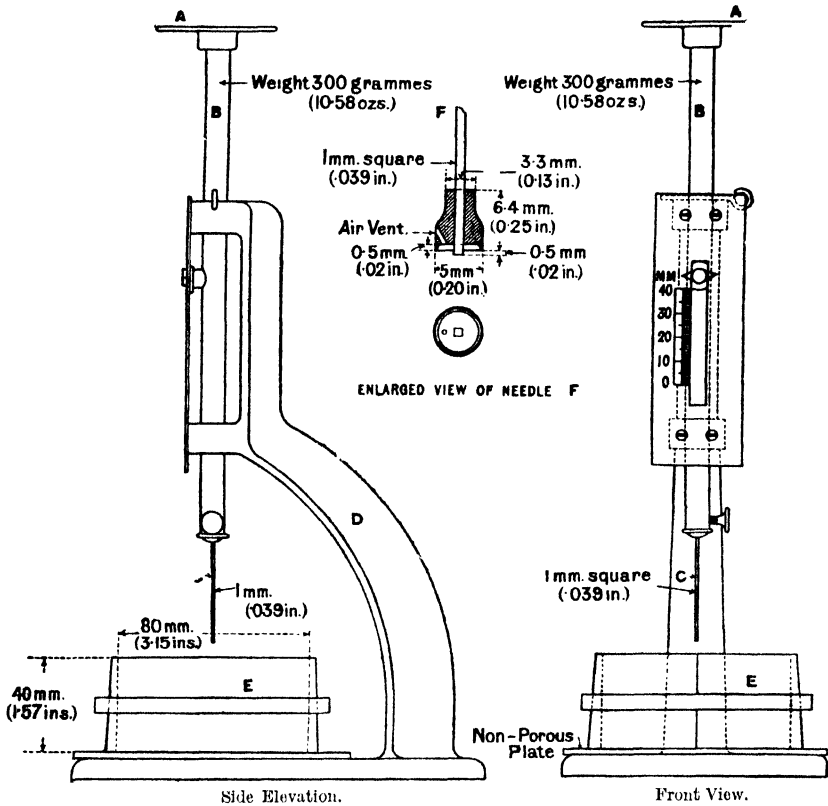



FIG. 61.—VICAT NEEDLE APPARATUS FOR ASCERTAINING SETTING TIME OF CEMENT.

needle makes an impression on the surface of the pat, but the circular attachment fails to do so. The period elapsing between the first addition of the water and this point is referred to as the Final Setting Time.

As temperature has much influence on the rate of setting, it is necessary to carry out all tests of this nature at a uniform and common temperature. The range 58° to 62° F. is usually specified for this purpose. The British Engineering Standards Specification states that a normal setting cement must have an initial set of not less than

twenty minutes and a final set of not more than ten hours. If a specially quick setting cement is specified or required, it shall have an initial setting time of not less than two minutes and a final setting time of not more than thirty minutes.

Tests for Soundness.—The soundness test for cement is of paramount importance, since it represents a rapid means of ascertaining the reliability of the material. The methods more generally classified under this heading are those which test constancy of volume, and for this purpose accelerated or boiling tests are applied in order to ascertain whether the cement is free from undue expansion or contraction. The accelerated tests generally used are those which subject the cement or block to the action of steam or boiling water. It has been frequently contended that these tests expose the cement to highly artificial conditions, which are not found in the natural use of the material, and that the results they yield are not always above suspicion. While it may sometimes happen that a hot test will reject suitable material, there is no doubt that if a cement is in the slightest degree unsound, the test will at once detect and emphasise the weakness, hence it should never be omitted.

Le Chatelier Test. The method generally used in Great Britain and which has been incorporated in the specifications of the British Engineering Standards Association is that of Le Chatelier. It has also been adopted in the specification of the Ministry of Public Works in France. The apparatus is shown in Fig. 62. It consists of a split cylinder made of spring brass or other suitable metal 0·5 mm. (0·019 in.) in thickness; the dimension of the mould and the distance of the indicators, A, A, from the centre of the cylinder are given in the illustration.

The test is carried out by placing the mould upon a small glass plate and filling it with cement gauged to a plastic condition, keeping the edges of the mould together during the operation. The mould is then covered with another glass plate upon which a small weight is placed, and the whole immersed for twenty-four hours in water at the normal temperature (58 to 62° F.). After measuring the distance between the indicator points the mould is placed in cold water, which is brought to the boiling point in about thirty minutes, and kept boiling for six hours. After cooling, the distance between the points is again measured. The difference between the two measurements represents the expansion of the cement, and should not exceed 10 mm. in cements that have been aerated for twenty-four hours, or 5 mm. with those that have been aerated for seven days.

Before being submitted to the above test the sample should be spread out to a depth of 3 inches and allowed to aerate for 24 hours in a temperature of from 58° F. to 64° F. Should the sample fail to

pass the test, a further test may be carried out on another portion of the same sample which has been aerated for seven days, under the conditions described above. The expansion on test should not exceed 5 mm.

Faija Test. This test is based on the principle that moist heat accelerates the setting of cement, and that a pat kept under these conditions for a few hours will have all the characteristics of a pat kept under normal conditions for several days. When tested in this

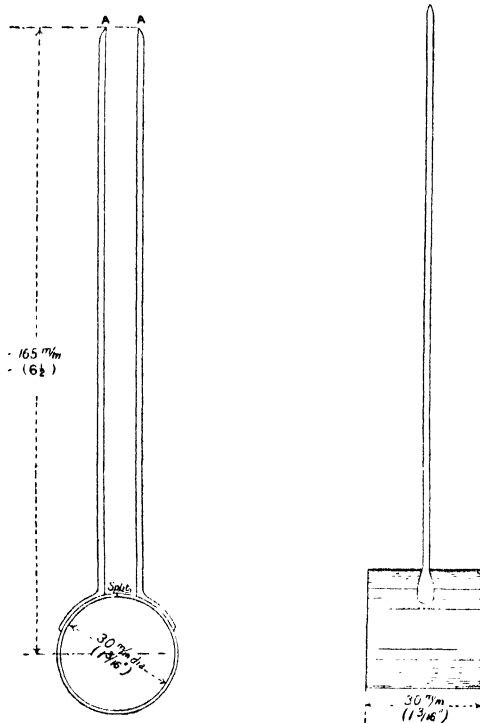



Fig. 62.

manner a sound cement attains great hardness, whereas an unsound material with a tendency to blow will develop this feature in a few hours. The test is conducted in a closed vessel containing water at a temperature of 110° to 115° F.; the space above the water is therefore filled with vapour arising therefrom, and is at a temperature of about 100° F. Immediately the pat is gauged it shonld be placed on the rack in the upper part of the vessel, and in five or six hours it may be placed in the warm water and left therein for nineteen or twenty hours. If at the end of that period the pat is still fast to the glass, or exhibits no sign of blowing, it may be considered perfectly sound; if, however, any signs of blowing appear the cement should

be laid out in a thin layer for a day or two and then retested, as the blowing tendency may disappear on aeration. The apparatus is illustrated in Fig. 63.

United States Specifications. Three tests are included in these specifications, one of which is a normal test, the remainder being accelerated tests. These tests do not include a quantitative measurement but rely entirely upon the judgment of the observer.

Three pats of neat cement are made and spread on glass plates. The pats should be about 3 in. in diameter, half an inch in thickness

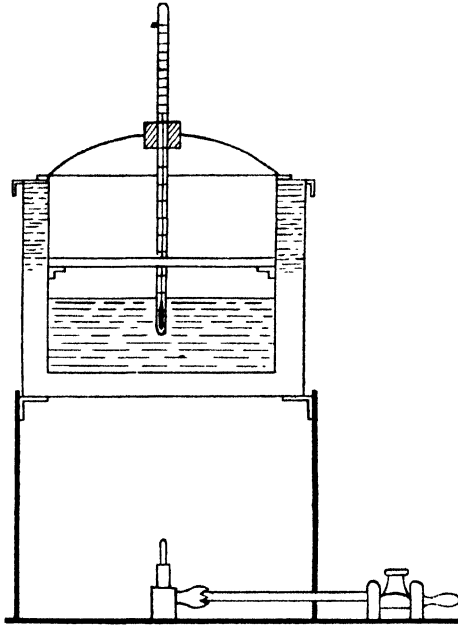



FIG. 63.

at the centre, and tapering to a thin edge. They are kept in moist air for a period of twenty-four hours, and then treated as follows:—

(*a*) A pat is kept in air at normal temperature and observed at intervals.

(*b*) A pat is immersed in water maintained as near 21° C. (70° F.) as possible for twenty-eight days, and observed at intervals.

(*c*) A pat is exposed in any convenient way, in an atmosphere of steam above boiling water, in a loosely closed vessel, for three hours.

To pass these tests satisfactorily, the pats should remain firm and hard and show no signs of cracking, distortion, or disintegration. Should a pat leave the plate, distortion may be best detected with a

straight edge applied to the surface which was in contact with the plate. In making the pats the greatest care should be exercised to avoid initial strains due to moulding, or too rapid drying out during the first twenty-four hours. The pats should be preserved under the most uniform conditions possible, and rapid changes of temperature should be avoided.

German Specifications. The general opinion in Germany does not favour the use of accelerated tests for soundness, as in other countries. This is due to the results of an inquiry instituted by the German Union of Cement Manufacturers, to ascertain how far the practical use of employing cements in construction coincided with the verdict of accelerated tests. The following is the opinion expressed by Mr Gary, who represented the laboratory throughout the inquiry.

Cements, all of which failed to pass the boiling test, were procured from ten different manufacturers, in various parts of Germany, under conditions of entire secrecy. These were tested immediately on receipt in three different laboratories, and portions of each were also used in the preparation of cement wares to be exposed to the weather. The laboratory results showed some variations due to different experimenters but upon the whole were considered satisfactory, while the practical work, consisting of medallions, pipe caps, etc., set hard, and capably resisted the exposure to the weather. Apart from minute hair cracks, all the objects, after two years' exposure, were found to be "still sharp cut and in good condition."

As a result of these experiments an accelerated test for constancy of volume was omitted from the specifications of this country. The decisive test is that a pat of neat cement, prepared on a glass plate, and protected from too rapid drying, immersed in water at the end of twenty-four hours and kept under constant observation for a period, exhibits no tendency to curl up or become cracked at the edges. In carrying out the test, the cement should be placed in water until it has become completely set. Quick setting cement may set under the twenty-four hour limit allowed, when the pat may be transferred to the water somewhat earlier, but in the case of slow setting cement the period should not be curtailed. The pats of slow setting cement must, until the setting process is completed, be protected from rapid drying. This may be done by placing them in a covered box. Thus the formation of hair-cracks due to speedy drying is avoided. These usually appear in the centre of the pat, and to unskilled observers might appear to be cracks caused by blowing. The appearances due to blowing can generally be detected after about three days' time. With favourable tests observations over a period of twenty-eight days are sufficient.

MECHANICAL TESTS FOR PORTLAND CEMENT

The utility of Portland cement is mainly due to the very considerable strength which it attains after the initial setting, either neat or with admixtures. The testing of the strength of Portland cement may be performed by either compressive or tensile tests.

Although in practice cement is rarely subjected intentionally to tensile strains, it is nevertheless customary in this country, and in the United States, to regard the tensile test as the standard, chiefly on account of the ease with which it may be applied. For tests of tensile strength small machines of moderate cost are suitable, while, for those by compression, large and costly machines are necessary. This has probably to some extent influenced the retention of tensile tests. In addition there is a fairly definite relation between compressive and tensile tests, usually regarded as about 10 to 1, hence variations in tensile strength will indicate corresponding (though much greater) variations in compressive strength.

A. Tensile Strength

The object of the tensile test is to determine the greatest stress per sq. in. which, under given conditions, the cement can be made to stand without rupture. It should not be forgotten that this test offers greater scope for variations, due to personal characteristics of the tester and to local conditions, than any of the other tests applied; hence the most scrupulous care must be observed in its manipulation, and so far as possible all operations involved should be reduced to a standard basis. The average tensile test of a modern neat cement is from 600 to 700 lb. per sq. in. at seven days, and 800 to 850 lb. in twenty-eight days, these periods having been generally adopted for testing. It is customary to carry out two series of tensile tests, one being on the neat material, and the other on an admixture of cement and sand in the proportion of 1 part by weight of cement to 3 parts by weight of sand. The use of a neat test is sometimes criticised on the ground that the full cementitious power of the material never comes into operation. It has been found that a coarse material will, in a neat tensile test, give results equal to a fine material, whereas with tests carried out on 3 to 1 sand and cement mixtures the superior constructive value of the finer material is clearly shown.

Test for Tensile Strength (Neat Cement).—The following extract from the British Engineering Standards Specification for Portland cement indicates the general procedure for this test.

The breaking strength of neat cement shall be ascertained from briquettes of the shape shown in Fig. 64.

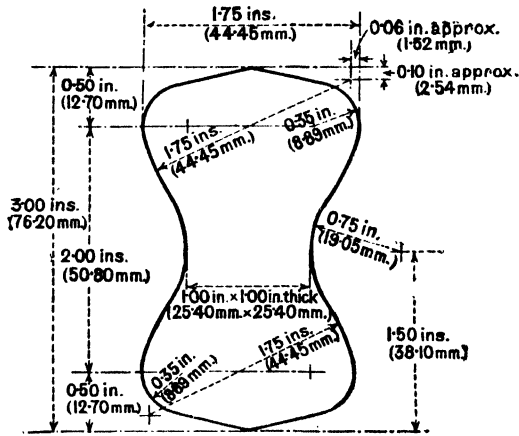
Preparation of Briquettes. Before being submitted to the test the sample should be spread out to a depth of 3 inches and allowed to aerate for twenty-four hours in a temperature of from 58° F. to 64° F. The cement shall be mixed with such a proportion of water that the mixture shall be plastic when filled into the moulds used for forming the briquettes. The cement gauged as above shall be filled into the moulds of the form required to produce briquettes of the shape shown in the illustration, each mould resting upon a non-porous plate. In filling the moulds the operator's hands and the blade of the ordinary gauging trowel shall alone be used. The trowel shall weigh about 7½ oz. (212·62 g.). No ramming or hammering in any form will be permitted, nor shall any instrument or apparatus other than the trowel

Briquette to have a uniform thickness of 1 in. throughout.

FIG. 64.—DIMENSIONS OF STANDARD BRIQUETTE

before described be employed for this operation. The moulds after being filled may be shaken to the extent necessary for expelling the air. Clean appliances shall be used for gauging, and the temperature of the water and that of the test room at the time when the above operations are being performed shall be from 58° to 62° F. (14·4° to 17·8° C.). The briquettes shall be kept in a damp atmosphere for twenty-four hours after gauging, when they shall be removed from the moulds and immediately submerged in clean fresh water and left there until taken out for breaking. The water in which they are submerged shall be maintained at a temperature of between 58° and 64° F. (14·4° to 17·8° C.). After they have been so taken out and until they are broken, the briquettes shall not be allowed to become dry.

Breaking. Six briquettes shall be tested for breaking strength seven days after gauging. The breaking strength shall be the average tensile breaking strength of the six briquettes. The briquettes

to be tested shall be held in strong metal jaws of the shape shown in Figs. 66 and 67, and the load shall be steadily and uniformly applied, starting from zero, and increased at the rate of 100 lb. per sq. in. of section (7·03 kg. per cm.) in twelve seconds.

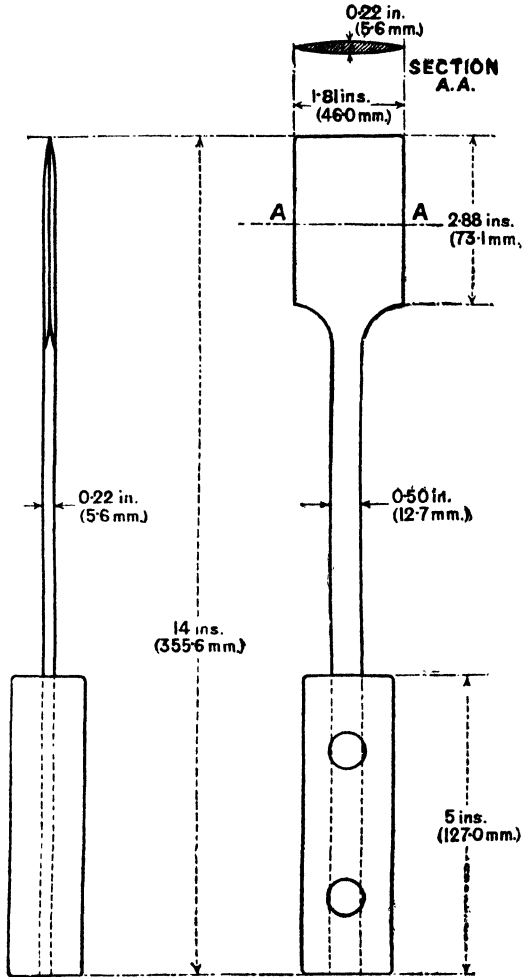



FIG. 65.—STANDARD SPATULA.

The breaking strength of the briquettes at seven days after gauging shall not be less than 600 lb. per sq. in. of section (42·18 kg. per sq. cm.).

Test for Tensile Strength (Cement and Sand).—The breaking strength of sand and cement shall be ascertained from briquettes also of the shape in Fig. 64. The briquettes shall be prepared in the following manner.

Preparation of Briquettes. A mixture of cement and sand in the proportion of one part by weight of cement to three parts by weight of the standard sand specified shall be gauged with water, the percentage of water to be used being determined by the following formula :—

$$\frac{1}{4}\,P + 2.50,$$

where P is the percentage of water required for the preparation of neat cement briquettes.

The mixture gauged as above shall be evenly distributed in moulds of the form required to produce briquettes of the shape shown in Fig. 64, each mould resting upon a non-porous plate. After filling a mould, a small heap of the mixture shall be placed upon that in the mould and patted down with the standard spatula shown in Fig. 65 until the mixture is level with the top of the mould. This last operation shall be repeated on the other side and the mixture patted down until water appears on the surface; the flat only of the standard spatula is to be used, and no other instrument or apparatus is to be employed for this operation. No ramming or hammering in any form will be permitted during the preparation of the briquettes, which shall then be finished off in the moulds by smoothing the surface with the face of the trowel. Clean appliances shall be used for gauging, and the temperature of the water and that of the test room at the time when the above operations are being performed shall be from 58° to 64° F. (14·4° to 17·8° C.).

The briquettes shall be kept in a damp atmosphere for twenty-four hours after gauging, when they shall be removed from the moulds and immediately submerged in clean fresh water, and left there until taken out for breaking. The water in which they are submerged shall be renewed every seven days and maintained at a temperature of between 58° and 64° F. (14·4° to 17·8° C.). After they have been so taken out and until they are broken, the briquettes shall not be allowed to become dry.

Breaking. The briquettes shall be tested for breaking strength seven and twenty-eight days respectively after gauging, six briquettes for each period. The breaking strength shall be the average tensile breaking strength of the six briquettes tested for each period. The briquettes to be tested shall be held in strong metal jaws of the shape shown in Figs. 66 and 67, and the load uniformly and steadily applied starting from zero and increased at the rate of 100 lb. per sq. in. of section (7·03 kg. per sq. cm.) in twelve seconds.

The breaking strength of the briquettes at seven days after gauging shall not be less than 325 lb. per sq. in. (22·85 kg. per sq. cm.) of section. The breaking strength of the briquettes at twenty-eight days after gauging shall show an increase on the breaking strength at seven days,

and shall not be less than the number of lb. per sq. in. of section arrived at from the following formula:—

$$\text{Breaking strength at seven days} + \frac{10{,}000}{\text{Breaking strength at seven days}}.$$

The specifications of the United States require a load increase of

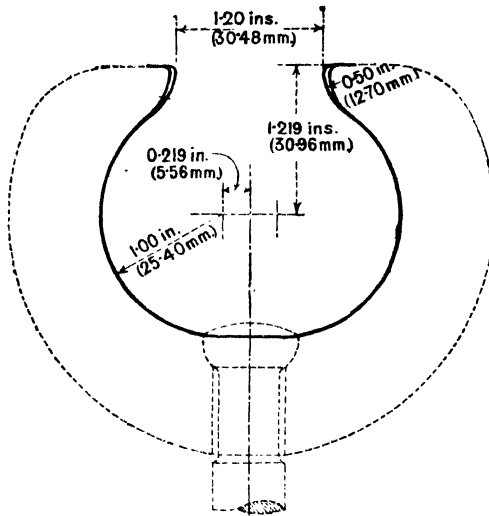



Fig. 66.

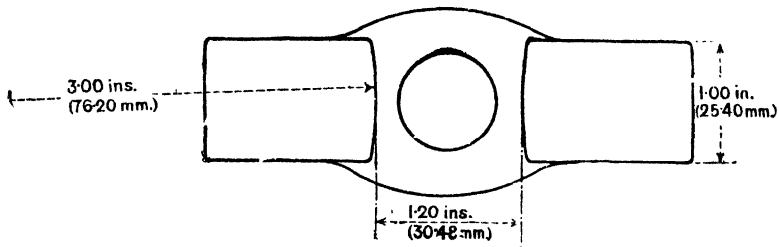



Fig. 67.—Elevation and Plan of Jaws for Holding Briquette.

600 lb. per minute and a minimum tensile strength at seven days of 200 lb. per sq. in. and at twenty-eight days of 300 lb. per sq. in.

Standard Sand. It has long been recognised that the nature of the sand used in the preparation of mortars has a very marked effect on their ultimate strength, hence the introduction of a clause governing the source and size of this material. The particulars are as follows.

The standard sand shall be obtained from Leighton Buzzard, shall be of the white variety, and shall be thoroughly washed and dried. Its loss in weight on extraction with hot hydrochloric acid shall be not more than 0·25 per cent. The sand shall pass through a sieve of

20 × 20 meshes per sq. in. (62 meshes per sq. cm.), and be retained on a sieve of 30 × 30 meshes per sq. in. (140 meshes per sq. cm.). The sieves shall be prepared from wire-cloth, which shall be woven (not twilled) and carefully fixed on the frames without distortion. The sieving area shall be not less than 50 sq. in. (322·58 sq. cm.), and the depth of the sieves shall be not less than 2¾ in. (69·85 mm.) measured from the surface of the wire-cloth.

30 × 30 Sieve. A standard 30 × 30 sieve is one having nominally an opening 0·0225 in. (0·572 mm.) in width, and 30 wires per lineal in. (25·40 mm.) of a diameter of 0·0108 in. (0·274 mm.). No sieve shall be regarded as standard which does not conform to these requirements within the following limits:—The number of wires in any lineal in. (25·40 mm.) shall be not less than 29½ nor more than 30½. No opening between adjacent parallel wires shall be more than 0·027 in. (0·69 mm.) in width. The diameter of any wire shall be not less than 0·01062 in. (0·2697 mm.) nor more than 0·01098 in. (0·2789 mm.).

20 × 20 Sieve. A standard 20 × 20 sieve is one having nominally an opening 0·0336 in. (0·853 mm.) in width, and 20 wires per lineal in. (25·40 mm.) of a diameter of 0·0164 in. (0·417 mm.). No sieve shall be regarded as standard which does not conform to these requirements within the following limits. The number of wires in any lineal in. (25·40 mm.) shall be not less than 19½ nor more than 20½. No opening between adjacent parallel wires shall be more than 0·0402 in. (1·021 mm.) in width. The diameter of any wire shall be not less than 0·01613 in. (0·4097 mm.) nor more than 0·01667 in. (0·423 mm.).

To carry out the test, dry the sand at 100° for one hour, weigh out 2 g. into a porcelain dish, add 1 c.c. of hydrochloric acid of specific gravity 1·16 and 20 c.c. of distilled water. Heat on the water-bath for one hour, filter, wash well with hot water, dry and ignite in a covered crucible.

Notes on Preparation of Briquettes. The value of the tensile strength test depends greatly on the preparation of the briquettes, and all precautions should be taken to eliminate the personal factor as far as possible. The cement and water should be mixed thoroughly, but at the same time as quickly as possible, and the moulds should be filled so that the material is solid and free from air spaces. Hand mixing is generally adopted in this country and in the United States, whereas in Germany the use of machines for mixing is favoured.

During the setting period of twenty-four hours prescribed in the specifications the test pieces should be adequately protected from draughts, otherwise lack of uniformity in results will ensue, due to uneven drying out. A simple form of storage consists of a wooden box zinc lined, and having a lid covered on the inside with thick

flannel, which is kept thoroughly moist during use. The percentage of water used in the gauging of neat briquettes is generally between 18 and 25, the proportion varying according to the age, fineness, and activity of the sample. It will be noted that the proportion of water required by the specification is such that "the mixture shall be plastic when filled into the moulds used for forming the briquettes." This in itself permits the introduction of a strong personal factor, and the desirability of a standard of consistency more definite than that of the personal observation of the manipulator is undoubtedly great. For sand and cement mortars the formula specified automatically incorporates the amount of water used for the neat cement pastes. The specifications of many other countries include clauses which tend to eliminate this factor, and place the measurement of consistence on a more definite basis. The method favoured by the American Society for Testing Materials for measuring the consistence of cement pastes is that known as the Plunger Test.

Plunger Test for Normal Consistence. For this test the Vicat needle, with a modified form of plunger, is adapted. A rod 1 cm. in diameter is substituted for the needle normally used for carrying out setting time tests. To carry out a determination, the cement paste, having been mixed, is filled into a non-porous mould 7 cm. in diameter and 4 cm. high, resting on a non-porous plate. Any excess of paste above the top of the mould is sliced off by a single oblique stroke of a trowel held at a slight angle to the mould. The paste confined in the mould is then placed under the rod, which is brought in contact with the surface and gently released. The cement is considered to be of correct consistence when the plunger settles to a point 10 mm. below the original surface of the paste, one half minute after release.

It is necessary to make up a series of trial pastes with varying percentages of water until correct consistence is obtained. Having determined the normal consistency of the cement, the amount of water required of the cement and sand mortar briquettes is found from a table.

Böhme Hammer Method for Cement-Sand Mortars. This method has been favoured in Germany for many years. It was designed by Professor Böhme and uses the minimum amount of water which enables the sand mortar to be formed into a briquette by the action of a hammer. The amount of water is assumed to be correct when between the 90th and 110th blow, liquid just begins to flow out of the notches of the filling box. The hammer head, which weighs 4½ lb., forms the head of a long arm of a lever, and the short arm is periodically depressed by projecting cams on the rim of wheel. When depressed to the fullest extent, so that the hammer is at the top of its stroke,

the short arm slips from a cam and the head falls by its own weight on to the anvil block piston of the mould. The wheel has 10 cams and is revolved at such a rate that the blow is delivered every second.

In addition to the methods detailed above, numerous formula have been devised for determining the amounts of water for mixing sand mortars, but these have not come into general use. Details of these, together with a discussion of the varying factors governing the

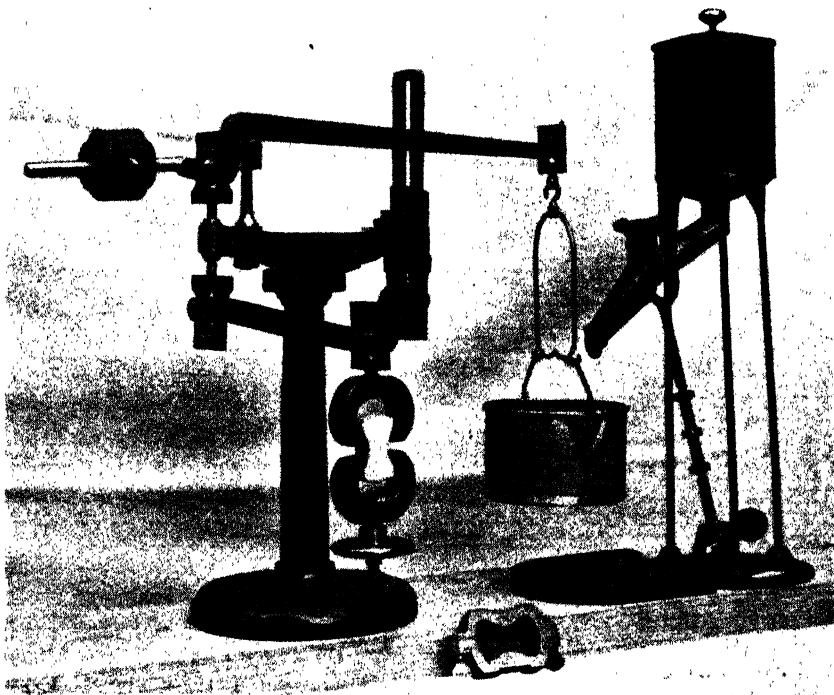



Fig. 68.

consistence of cement pastes and mortars, are to be found in an excellent pamphlet published by the Building Research Board (see Literature, p. 382).

Salter's Testing Machine.—This apparatus (Fig. 68) fulfils the necessary requirements, and is frequently used in this country. It consists of a japanned cast-iron frame, carrying a pair of compound levers. The lower lever has a ratio of 5 to 1 between its arms, and the upper one of 10 to 1, so that the combined leverage is 50 to 1, and the load on the briquette is fifty times the weight of the loaded bucket. The levers are fitted with tempered steel knife edges, which rest on

polished concave bearings also of tempered steel, thus obtaining a very sensitive balance. A sliding balance weight is fitted to the upper lever to bring the levers into an initial state of equilibrium. The upper clamp to receive the cement briquette is suspended from a knife edge on the lower lever; the lower clamp is attached to the base of the column, and is adjustable by means of a screw and small hand wheel. The supply of shot to the bucket is automatically cut off the moment the briquette breaks.

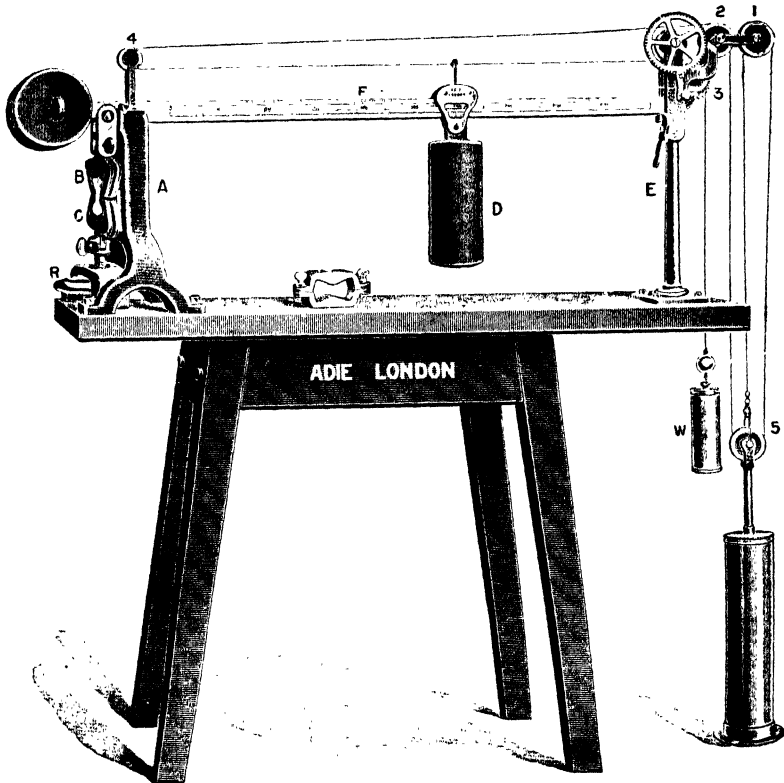



FIG. 69.

To use the machine, set the levers "floating" by means of the sliding balance weight. Once set tightly, this need not be touched. If, however, it is desired to start the load from zero, this weight can be adjusted to balance the weight of the cam by running it out to the end of the lever. In that case either 50 lb. must be deducted from the scale when weighing the shot and cam, or to save calculation the pointer of the balance can be adjusted by a screw incorporated for that purpose so as to stand at zero with the weight of the cam, and in that case the pointer will give the weight of the shot only.

To commence a test the briquette is first of all fixed in the clamps

as centrally as possible. The bucket is then hung on the bridle, and the hand wheel screwed up until the top side of the lever from which the cam is suspended is about half an inch from the top of the guide. This allows ample downward movement if the clips slide up the briquette as the load is increased, and prevents the lever touching the bottom of the guide before the rupture. The handle is then depressed to the first notch. As soon as the briquette is broken, the bucket falls on to the rubber pad and depresses the lever by which the shutter is released, thus cutting off the supply of shot. The bucket is removed and placed on the spring balance by which the breaking load is at once indicated without calculation ; the shot should be of uniform size, No. 6 for preference.

Adie's Testing Machine (Fig. 69).—This is one of the oldest, and at the same time best known machines in this country. The makers claim that the aim in construction has been to secure the most accurate and reliable results, with absolute permanence and non-interference from the hand of the operator ; thus all springs and screws are dispensed with, and the simple steel lever and vernier (with weight attached), travelling on rollers, adopted, the vernier being moved along the lever by a cord passing over pulleys fixed to standards, the hand not touching or in any way affecting the lever during testing. To make this more unquestionable, in addition to the speed reducing wheel and pinion, an automatic regulator can be added. In addition to compound levers spring balances have been eliminated, thus reducing the liability to multiplied errors.

To test the briquette, insert it in the clips B and C, then turn the wheel R until the lever at E rises well above the zero line. The handle on the standard E is turned, when the weight D is moved along until the briquette has broken. With the more improved type of machine an automatic regulation is incorporated by means of which a uniform rate of travel of the weight is ensured so that all tests are carried out at an equal number of lb. per minute. The regulation is self-acting, and once a test has been commenced no further control is necessary. Moreover, directly the briquette is broken the weight is held in position by means of a clutch. The rate of travel of weight may also be varied if desired.

To use the automatic regulator, see that the vernier is at the commencement of the scale, then place the briquette into its place, tighten by the wheel R until the strain is sufficient to lift the lever well above the zero line on the standard E, then hang on brass weight W, which will at once commence to move the vernier along the lever ; see that the vernier weight does not rock while travelling. To commence another test, remove weight W, lift the lever by means of the lifter, which is fixed to the standard E, then press in the cross

handle at the top of the piston rod, which will let the piston down gently, and return the vernier to commencement of scale, and proceed as already described.

B. Compressive Strength

The compressive strength of a cement or concrete is of direct practical importance, for these materials are rarely subjected to any other type of strain when used in actual work. In Germany this is the standard test for the strength of cement and is preferred to the tensile test. It is rarely necessary to determine the compressive strength of neat cement, as such a test is no guide to the quality of concrete which any specific cement would produce. This point is emphasised in the German Standard Specifications in the following extract:—

"Because it is not possible to judge uniformly of the capacity of the cement for uniting sand particles by means of tests conducted with neat cement—namely, when it is necessary to compare samples of cement obtained from different factories—it is laid down that the testing of the cohesion of the cement should take place when mixed with sand."

Compressive tests require the use of heavy testing machines, and for this reason their use is not so general in this country as might be expected. On the continent the tests are carried out on 3 to 1 sand and cement cubes having an edge of about 2¾ in. The materials are mixed with water and stored in the customary manner, *i.e.* one day in moist air and then immersion in water until the time specified for the test.

An excellent machine for carrying out compressive tests is the hydraulic apparatus of Amsler Laffon of Schoffhausen, Switzerland. This machine is capable of testing up to 60,000 lb. compression. The cubes are held between two compression plates, the lower of which rests on the piston contained in the main cylinder. The upper plate just touches the flat end of the screw spindle, this being used only to set the distance between the plates to the size of the test block. During the test the upper plate is at rest and the pressure is applied upwards through the lower plate from the piston. This in turn is actuated by the action of a viscous oil coming from a plunger pump, driven by the handle shown in the right of the illustration. The gauge is a column of mercury, communicating with a pressure reducing cylinder. The pressure is then measured by the height of the column. The machine is extremely robust and in accuracy is equal to any good lever machine.

The periods of testing are usually seven days and twenty-eight days. The German Specifications require a minimum compressive strength at seven days of 1706·76 lb. per sq. in., and at twenty-eight days a minimum of 3555·75 lb. per sq. in.

C. Transverse Tests

This test has received no official recognition in the specifications of this country, but is nevertheless frequently used by engineers and others having supervision of concrete work. The simplicity of the apparatus, the ease with which the test may be conducted, and with which it lends itself to varying sizes of test specimens undoubtedly accounts for its popularity.

The simplest arrangement is two knife-edges on which to rest the test specimen, and a means of applying the load to the centre of the bar. The bending stress is usually found to be from 1½ to twice the tensile stress, hence it is usually desirable to incorporate a lever arrangement whereby the weights are multiplied. The only precaution

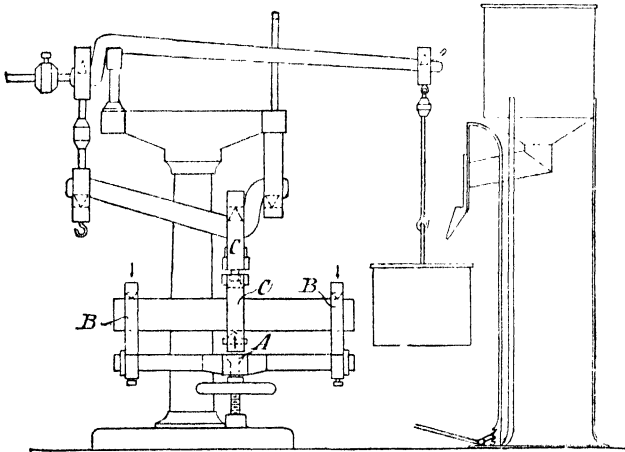



FIG. 70.

necessary in this case is that the load must be applied perpendicularly, and at right angles to the axis of the test specimen.

If desired the tensile testing machine may be employed for this test, after being fitted with the auxiliary mechanism shown in Fig. 70. This consists of a strong steel bridge, A, which is fixed to a screw held in a ball-socket and occupies the position of the lower clip in the original apparatus. At each end of the bridge are oblong carriers, B, B, in which are knife-edges which hold the ends of the briquette. Half-way between these is the third point of contact, a knife-edge fixed in the stirrup C and pressing against the under side of the test piece. By applying weights to the levers, force is exerted at C, until the test piece is snapped. The distance B, B, and the section of the briquette are of standard dimensions. Under ordinary circumstances a briquette of 4 × 4 sq. cm. sectional area is used, which has the advantage of being suitable for the crushing test after being broken; the distance

between the outer knife-edges is 256 mm. Under these conditions the bending strain will be thirty times the load applied to the levers, working at the factor 50. The carriers, B, B, can be moved inwards along the bridge until they are 100 mm. apart; in this position they serve for small briquettes of 2 × 2 sq. cm. section. For such cases the central knife-edge must be raised 2 cm.; for this purpose it is constructed to slide between vertical grooves, so that it is merely necessary to place a steel block 2 cm. thick underneath it.

It is found, as a rule, that the bending strength of a cement is about double the tensile strength.

An excellent bending test apparatus has been adapted by Amsler-Laffon to their crushing machine, by means of which a maximum strain of 5000 kg. can be produced.

ADULTERATIONS OF PORTLAND CEMENT

The manufacture of Portland cement has been so simplified and cheapened of late years that adulteration would seldom be remunerative. Blast-furnace slag is practically the only substance that is likely to be used as an adulterant, and the chemical composition of this material is so similar to that of Portland cement that its detection by analysis is difficult. Many attempts have been made to limit the term "Portland cement" to a product obtained from certain materials manufactured by definite processes. Practically no cement is now made in the same way as that produced by Aspdin the inventor, who first called his material "Portland cement." Strictly speaking, therefore, no cement now in the market is real "Portland" as defined by its originator; but consumers understand by the term a product possessing certain definite properties, and any mixture departing materially from the recognised standard should have its composition declared to the purchaser.

In order to obtain a process for detecting an admixture of blast-furnace slag with Portland cement, a special investigation was carried out by R. and W. Fresenius for the Association of German Portland Cement Manufacturers; but the chemical tests proposed were not considered conclusive, and were not adopted as standards.

The best means of detection is Hauenschild's flotation test, which is conducted according to Loebell's method, as follows:—The cement is first submitted to Fresenius' permangate test, and its reducing effect determined. If 1 g. of the sample requires not more than 3 mg. of potassium permanganate, the absence of blast-furnace slag may be assumed. If a greater quantity is reduced, the material may consist either of (1) rotatory kiln cement, (2) cement mixed with blast-furnace slag, or (3) cement to which slag has been added before

calcination. It is then advisable to make an analysis by flotation. For this purpose the cement is sifted through a sieve of 2500 meshes to the sq. cm. and 10 g. of the fine material stirred up with benzene in a flat crystallising dish and washed so as to remove the very finest dust; the residue is dried at 100°. To prepare the separating liquid, about 50 c.c. of methylene iodide (dried over calcium chloride and filtered through Portland cement which has been recently ignited and kept in a desiccator) is placed in a cylinder surrounded by water at 15°, and rectified oil of turpentine (dried over calcium chloride and filtered) added drop by drop and well mixed until the specific gravity of the liquid is 3·010. The liquid is kept in a yellow bottle to protect it from the action of light. This mixture is much less sensitive to light than a methylene iodide-benzene mixture, to which it is superior in other respects. To carry out the test a dry separating funnel of about 70 c.c. capacity (Fig. 71), the stop-cock of which has been greased with vaseline, is charged with 40 to 50 c.c. of the separating liquid, and 5 g. of the prepared cement is introduced by means of a short-stemmed funnel. The separating funnel *t* is thoroughly shaken and evacuated to about 17 mm. of mercury by means of the filter-pump *n* during about five minutes; the evacuation should not be prolonged beyond this period, as otherwise some turpentine may evaporate and cause the liquid to change its density. It will be found necessary to open the pinchcock *g* from time to time, in order to guard against excessive frothing. The funnel, which must be carefully stoppered, is then laid on its side, gently agitated by rocking, and allowed to remain (protected from light) for a short time, until the lighter solids have collected at the top of the liquid and the heavier have settled at the bottom; the funnel is then held at the neck and very slowly raised into a vertical position. By proceeding in this manner, the lighter and heavier particles are enabled to pass one another, and those light partieles which are retained by the heavy ones are given time to disengage themselves and to rise to the surface. A single treatment of the cement with the separating liquid thus affords an approximately quantitative separation of the constituents. The cement which sinks to the bottom is cautiously transferred to a Gooch crucible, in which it is dried and weighed. In fitting up the crucible, a layer of chemically purified, long fibre asbestos is laid on the bottom of the crucible, then

Fig. 71.

a layer of short fibre asbestos, then a porcelain filter plate, and finally another layer of short fibre asbestos. The crucible is then fitted up in the usual way, the layer of asbestos washed with distilled water and the crucible dried at 110° and weighed. The separated cement is then filtered off. The clear methylene iodide mixture is removed from the filter flask and the residue in the crucible washed with absolute alcohol, benzene, and finally with ether, alternately, with and without suction. The crucible and its contents are dried at 110° and weighed, and the cement then subjected to chemical analysis.

The slag, which rises to the top of the separating liquid, is similarly treated. It is not desirable to use more than 5 g. of material for the valuation. The separating liquid must be readjusted to a density of 3·010 before each experiment, since a portion of the turpentine evaporates during filtration. To recover the methylene iodide, the united washings are distilled to expel the less valuable solvents, and the residue cooled to 5°; the iodide then separates out in white scales, from which the brown mother liquor is poured away. Under the action of light the distillate will be found to assume a pink tint due to a separation of iodine; this can be removed by shaking with and subsequently distilling over mercury, as mercuric iodide is soluble in the mixture of liquids used in the washing. It is imperative to follow the above directions exactly if good results are to be obtained.

The products separated are:—

1. *Light Materials*, which float on the liquid and which may consist of:—

Carbon, average sp. gr. 1·39.
Gypsum, sp. gr. 2·33.
Coal-ash, average sp. gr. 2·73.
Blast-furnace slag, average sp. gr. 2·94.

These can be further separated from one another by treatment with suitably adjusted methylene iodide-turpentine mixtures.

2. *Heavy Materials*, which sink in the liquid and which may consist of:—

Cement, average sp. gr. 3·035.
Particles of iron, sp. gr. above 3·01.
Carbides from the slag, sp. gr. above 3·01.

These can also be separated by means of suitable liquids.

Chemical analysis of the separate portions yields trustworthy information as to the presence of slag. According to Tetmajer, blast-furnace slags of the most varied origin contain 27·31 to 39·95 per cent. SiO_2 and 25·24 to 50·67 per cent. CaO, whilst the limits for Portland cement are 19 to 26 per cent. SiO_2 and 57 to 66 per cent. CaO.

RAPID HARDENING PORTLAND CEMENT

This type of cement has been introduced in recent years to meet the growing demand for a material with rapid hardening properties which would enable certain types of constructional work to be greatly accelerated. It should not be confused with quick setting cements which require great rapidity of mixture and subsequent handling, but may be mixed and handled in exactly the same way as ordinary Portland cement.

The rapid hardening properties are imparted by slightly increasing the proportion of alumina, and by extremely fine grinding of the resultant clinker. The former factor is sometimes entirely dispensed with, and the rapid hardening properties obtained by simply continuing the grinding of the clinker for a much longer period than for normal products.

As a rule rapid hardening cements give a residue on a 180 × 180 cement sieve of between 1 and 2 per cent. It has not been thought necessary as yet to introduce a separate specification for this type of material, and the method of testing and analysis are precisely the same as for normal Portland cement. A point which is sometimes raised is the unnecessary severity of the tensile test of the British Standard Specifications when applied to these materials. Thus, if by a modification in the manufacture the strength is developed at an early date, it is perhaps unreasonable to demand an appreciable increase at later dates. This point is met to a certain extent in the specification, by the inclusion of a formula which reduces the required growth from seven to twenty-eight days as the seven-day test increases. Even so should the allowance not prove adequate in certain cases, the total rejection of the cement would be an unnecessarily severe penalty.

PORTLAND BLAST-FURNACE CEMENT

The use of blast-furnace slag as a pozzolanic addition to Portland cement has already been mentioned, and an important group of materials composed of these ingredients is now marketed under the name of the Portland blast-furnace cement. The enormous quantity of blast-furnace slag produced annually and discarded as waste product has long been regarded as a potential source of a cheap cement, and much research work has been directed with a view to its utilisation for this purpose.

One process which has been used with considerable success, and which we believe is still carried out in certain parts of the United States, is that of roasting together an intimate finely-ground mixture of the slag and limestone in definite proportions. In this country the manufacture of slag cement is carried out by grinding together Portland cement clinker and granulated slag previously mixed together in definite proportions. One of the most successful methods of

granulating blast-furnace slag is that invented by Dr Colloseus of Berlin. The method consists in pouring a steady stream of the molten slag, as tapped from the furnace, out of a ladle on to a rapidly rotating drum suitably encased in the granulator. Just before striking the drum the slag is made to pass through a jet of water containing magnesium sulphate in solution, and the grains thus formed are prevented from clinkering together by impact with the drum. The granulated slag passes by a chute to conveyors, which deposit it in the cooling and storing sheds.

These cements find much application for work under water, more particularly sea water, where they show a high degree of resistance to the destructive action of magnesium sulphate.

Testing and Analysis. The testing and analysis of these materials present little difficulty, and they may be treated in exactly the same way as ordinary Portland cement. Their use is now of sufficient importance to warrant the issue of separate specifications by the British Engineering Standards Association,[1] with whose permission we are able to reproduce the following salient points.

Composition and Manufacture. This cement, hereinafter called "the cement," shall consist of a mixture of Portland cement clinker and granulated blast-furnace slag. These two materials may be mixed together in such proportions as the manufacturer may prefer, subject to the proviso that in no case shall the proportion of slag exceed 65 per cent. of the total quantity.

The Portland cement clinker shall be manufactured by intimately mixing together calcareous and argillaceous or other silica and alumina bearing materials, and burning them at a clinkering temperature. The granulated blast-furnace slag shall then be added to the Portland cement clinker and the whole ground together so that the two constituents, namely, the Portland cement clinker and the granulated blast-furnace slag, shall be thoroughly and intimately mixed, and shall produce a cement capable of complying with this specification.

Chemical Requirements. The chemical composition of the Portland cement clinker portion of the mixture must comply in all respects with the separate specification issued by the Association (see p. 338).

The slag cement must comply with the following conditions as to its chemical composition :—

Insoluble residue	not above	1·5	per cent.
Magnesia	”	5	”
Loss on ignition	”	3	”
Sulphur (as sulphide) . . .	”	1·2	”
Sulphur (as sulphuric anhydride) . .	”	2	”

[1] B.E.S.A., *Stand. Spec. for Portland Blast-furnace Cement*, 1926.

Of these clauses, that referring to the sulphur present as sulphide is usually the most difficult to comply with, owing to the tendency for blast-furnace slags to carry large amounts of calcium sulphide.

Aeration of Sample. Before any sample is submitted to the tests described below, it should be spread out at a depth of 3 in. for twenty-four hours at 58° to 64° F.

Setting Time. The Vicat needle apparatus as described on p. 351 is applied to this test. The specification differentiates between two types of material, normal setting and quick setting. The former material must have an initial setting time of not less than thirty minutes and a final setting time of not more than ten hours. The latter material should have an initial setting time of not less than five minutes and a final setting time of not more than thirty minutes.

Determination of Fineness. The cement sieves as described on p. 346 are utilised for these tests. One hundred g. of cement is sifted continuously for a period of fifteen minutes on a 180 × 180 sieve, and for a period of five minutes on a 76 × 76 sieve, in the order of succession given below and with the following results:—

(*a*) The residue on the 180 × 180 sieve must not exceed 10 per cent.

(*b*) The residue on the 76 × 76 sieve must not exceed 1 per cent.

Test for Soundness. The soundness test is carried out by the method of "Le Chatelier." The apparatus has been described on p. 353. The expansion must not exceed 10 mm. Should the cement fail to comply with this test a further test may be carried out on a portion of the material which has been aerated for seven days.

Test for Tensile Strength:—

(a) *Neat Cement.* The briquettes are prepared in the manner described for Portland cement, the proportion of water used being such that the mixture is plastic when filled into the moulds. The briquettes are kept in a moist atmosphere for twenty-four hours after gauging, and then removed from the moulds and immediately submerged in clean fresh water until the time required for breaking. The breaking strength of the briquettes at seven days after gauging should be not less than 600 lb. per sq. in. of section.

(b) *Cement and Sand.* The mixture of cement and sand in the proportion of one part by weight of cement to three parts by weight of standard sand is gauged with water, the percentage of water used being determined by the formula—

$$\frac{1}{4} P + 2.50,$$

where P is the percentage of water required for the preparation of neat cement briquettes. The briquettes should be kept in a damp

atmosphere for twenty-four hours after gauging, and then removed from the moulds and submerged in clean fresh water until required for breaking.

Tests are carried out at seven and twenty-eight days respectively after gauging. The breaking strength of the briquettes at seven days after gauging should be not less than 325 lb. per sq. in. The breaking strength of the briquettes at twenty-eight days after gauging should show an increase on the breaking strength at seven days, and should be not less than the number of lb. per sq. in. arrived at from the following formula:—

$$\text{Breaking strength at seven days} + \frac{10{,}000}{\text{Breaking strength at seven days}}.$$

C. Gypsum Cements

An important group of materials resulting from the partial or complete dehydration of gypsum is being increasingly used for plastering. Pure crude gypsum is a hydrated sulphate of lime with a chemical formula $CaSO_4 2H_2O$. This corresponds to the composition

Lime (CaO)	32·6 per cent.
Sulphur Trioxide (SO_3)	46·5 „
Water (H_2O)	20·9 „

Plaster of Paris.—This is formed by calcining gypsum at temperatures between 212° and 400° F. A partially dehydrated product is formed having the formula $CaSO_4, \frac{1}{2}H_2O$. This corresponds to the composition:—

Calcium sulphate	93·8 per cent.
Water	6·2 „

If the plaster of Paris is manufactured from pure gypsum, it sets with great rapidity when mixed with water. The rapidity of set is, however, modified by the addition of borax or of certain organic compounds usually referred to as retarders. In addition plaster of Paris manufactured from impure gypsum containing appreciable amounts of clayey matter usually has slow setting properties.

Dead Burnt Plasters.—These are manufactured by calcining gypsum at temperatures above 400° F. The product so obtained was for many years regarded as having no cementitious properties, but it has become gradually appreciated that this supposition was fallacious, and that providing the product was finely powdered it was capable of setting to a hard mass when mixed with water. The setting is slow, usually taking at least ten hours.

Keene's Cement.—This is manufactured by first calcining gypsum and then steeping the product in a solution of cream of tartar and borax. This is dried, and again calcined at a red heat, cooled and

pulverised. The product is a very fine grained white powder. Numerous other patent products are now on the market, all of which are manufactured along very similar lines.

Analysis of Gypsum, Plaster of Paris, etc.

Silica and Insoluble Residue. 0·5 g. of the finely powdered material is dissolved in 30 c.c. of 1 : 3 hydrochloric acid and evaporated to dryness on the water-bath. The dish is heated for a short time at 120°, 20 c.c. of 1 : 1 hydrochloric acid is added to the dish, which is warmed for a few minutes, the contents filtered and the residue well washed with warm water. It is dried, ignited and weighed. It should be reported as above.

If an appreciable residue is noted, it may be fused with sodium carbonate and examined as for clay (p. 333).

Calcium Oxide. The filtrate from above is rendered ammoniacal and allowed to stand in a warm place for a short period. Any ferric oxide or alumina which separates out should be separated and determined in the usual manner. The separation of lime as calcium oxalate is then proceeded with (see p. 340).

Sulphuric Anhydride. 0·5 g. is treated with 50 c.c. of 1 : 5 hydrochloric acid and boiled for a few minutes, 100 c.c. of boiling water is added and the boiling continued for five minutes. The liquid is filtered hot and washed well with hot water. Fifteen c.c. of a 10 per cent. solution of barium chloride is added to the filtrate, and the beaker allowed to stand overnight. The barium sulphate is filtered off, washed with warm water and dried and ignited at a low temperature. It contains 34·3 per cent. of sulphuric anhydride.

Free Water. One hundred g. of the coarsely powdered material is dried at 70° to 80° for two hours.

Combined Water. A weighed quantity of about 1 g. of the dry sample is heated in a covered crucible at 215° to 230° to constant weight.

Testing of Gypsum Plasters

Methods of testing these products have never been standardised and the result is that each investigator applies such tests as he may deem advisable. In general the practice has followed closely along the lines of lime and cement testing.

Adjustment of Consistence of Gypsum Plasters

The consistence of gypsum plasters shall be adjusted to give standard spread to a mean diameter of 9·7 cm. when tested in the Southard viscosimeter (p. 312) immediately after gauging. Since

with rapid setting plasters an initial set, or at least a preliminary stiffening which will greatly affect the viscous flow thereof, may take place in the period necessary for a complete test according to this method, it can only be applied to (*a*) slow setting plasters, such as genuine Keene's cement, natural anhydrite, or hard-burnt plasters in general, with a setting time of two hours or more; (*b*) retarded plasters with a similar minimum setting time. For fast setting plasters of the plaster of Paris type a retarder of set must be used in the form of ½ per cent. *fresh* glue solution for gauging.

For similar reasons the plaster must be tested immediately after gauging, and the lengthy process of adjustment of consistence with repeated tests of consistence given for lime putties cannot be adopted here. Water may be added to an over-dry test sample, and the test for consistence repeated after thorough stirring; but the removal of excessive water from an over-wet sample should not be attempted, a fresh sample being taken instead. If additions of water have been made after the first gauging, the test must be repeated with the final proportion arrived at (or preferably about ½ per cent. less to allow for the intermediate losses in the earlier tests) to check the accuracy with a fresh sample of the plaster. Great care is necessary in cleaning out the viscosimeter after each test, on account both of the danger of caking of set plaster under the piston, and of the possible accelerating action of set plaster on subsequent samples under test.

Gauging the Sample. Eighty c.c. of clean water at laboratory temperature is poured from a graduated glass cylinder, containing altogether 150 c.c., into a clean vessel of a deep shape. Two hundred g. of the plaster sample, obtained in accordance with method (*b*) (p. 305) is then weighed out and poured into the 80 c.c. of water with continuous and rapid stirring so that all is effectively moistened.

The stirring is continued for two minutes, after which more water is cautiously added from the graduated cylinder, small quantities at a time and with constant stirring, until approximately the correct consistence is attained at which the plaster will just pour. The cylinder of the Southard viscosimeter is then filled, with the piston at its lowest point, by pouring in the plaster, care being taken to avoid forming air bubbles and to remove any that may have formed by cautious stirring of the plaster in the cylinder by a palette-knife or its equivalent. The plaster is then struck off with the knife smoothly at the top, and level with the plate. The surface of the plate should be clean around the cylinder rim after this operation.

The plaster is then ejected in the manner detailed on p. 313, and observing the same precautions. The "spread" of the plaster on the horizontal plate is then observed, the mean diameter being read off by the

aid of the concentric rings spaced at 1 cm. radial distance engraved on the plate. The standard spread of 9·7 cm. must be attained within 3 mm. (or about one-third of an interval). When the standard consistence has been obtained, the volume of water which has been used is read off on the scale of the graduated cylinder, and the water ratio recorded; (c.c. water used/wt. in g. of plaster used × 100 per cent.).

If the observed spread is less than standard, the material may be returned to the mixing vessel and thoroughly incorporated with the unused residue together with a small quantity of water added from the graduated cylinder, and then stirred for one minute; the test for spread on the viscosimeter is then repeated. If the observed spread is greater than standard, the whole gauging process must be repeated. using rather less additional water with fresh material. Whenever repeated adjustments over an extended period have been made, a final check must be made, as before indicated, by repeating the gauging with fresh material, using the ostensibly correct water ratio and operating as rapidly as is practicable.

The material of the final, correct sample may be used immediately for the preparation of briquettes for strength tests, but not for determination of setting times. All other gauged material must be discarded. For all subsequent tests fresh material must be used, gauged with the amount of water determined as above, and used immediately.

Adjustment of Consistence of Sanded Gypsum Mortars

These tests should be carried out on mortars containing three parts by weight of sand to one part by weight of the gypsum plaster. The standard sand used should fulfil the same requirements as for Portland cement mortars (see p. 361). The mortar should be adjusted to the same consistence as lime putties, *i.e.* to half-inch slump on the Southard viscosimeter.

Tensile Strength. The tensile test is conducted on briquettes of the same dimensions as are used for Portland cement. The briquettes should be stored in a cabinet with free access of air, but in such a manner as to be protected from draughts. Specifications issued in the United States require neat gypsum plasters to have minimum tensile strength of 150 lb. per sq. in. Plasters containing not more than two-thirds of sand should have a minimum tensile strength of 75 lb. per sq. in., and those containing not more than 75 per cent. of sand should have a minimum tensile strength of 50 lb. per sq. in.

These figures may be taken as indicative of the strengths obtained by this class of materials.

D. Aluminous Cements

Aluminous cements differ from Portland cement, and rapid hardening Portland cement, in that they contain a much higher proportion of alumina and much less silica. The percentage of alumina generally varies within the limits of 36 per cent. to 41 per cent., and the silica 4 per cent. to 10 per cent. A typical analysis is as follows:—

	Per cent.
Silica	6·05
Alumina	40·16
Ferric oxide	6·89
Ferrous oxide	5·23
Titanium oxide	1·94
Calcium oxide	39·38
Total	99·65

In addition the material may contain a small quantity of magnesium oxide and metallic iron.

The most important representative of this class of materials is known as "ciment fondu." The process of manufacture consists of mixing bauxite with lime or calcium carbonate in definite proportion, fusing the mixture in a blast furnace, cooling and grinding the slag to a fine powder. Bauxite does not exist to any great degree in this country, and hence must be imported. For this reason the cost of the finished material is higher than that of Portland cement.

On the other hand it possesses certain pronounced advantages. In the first place it possesses rapid hardening properties which enable constructional work to be greatly accelerated. At the end of twenty-four hours its strength equals that attained by the best brands of Portland cement in a month. It is, however, comparatively slow setting and may be worked in the usual manner. Secondly, it is extremely resistant to sea water, and to water containing gypsum, sulphate of magnesium, etc.

Chemical Analysis

Raw Materials. The analysis of limestone has already been dealt with (p. 294 *et seq.*), and that of bauxite on p. 7. It is common for bauxite to contain notable amounts of titanium oxide, hence a determination of this constituent should be made.

Ciment Fondu.—The following scheme of analysis, which is sufficiently accurate for general purposes, can be carried out in five to six hours.

Silica. Weigh off accurately 1 g. of the material and place in a porcelain basin, the bottom of which is slightly wet. Mix the cement

into a paste with a glass rod, and add 15 c.c. of concentrated hydrochloric acid. Stir well in order to prevent the cement from sticking to the bottom of the basin, and then place on a water-bath the water in which is just boiling. Allow to evaporate with occasional stirring until quite dry, but do not bake too much as this tends to render the titanium oxide and alumina insoluble.

Cool and add 40 c.c. of 1 : 1 hydrochloric acid and place on the water-bath for about ten minutes. Filter through a No. 31 Whatman filter-paper, wash three times with dilute hydrochloric acid, and finally with hot water until free from chlorides. The filtrate is reserved for the determination of alumina, etc. The filter paper and residue is transferred to a platinum crucible and ignited and weighed. A few c.c. of hydrofluoric acid is added to the crucible and three drops of sulphuric acid, and the whole evaporated to dryness, and again ignited and weighed. The difference between the two weights represents silica.

Ferric Oxide and Alumina. Any insoluble matter remaining in the crucible after the silica determination is fused with a little potassium bisulphate, and dissolved, and the solution added to the main filtrate. This is thoroughly cooled and made up to 250 c.c.

After mixing portions are taken as follows:—

50 c.c. for the determination of mixed oxides, lime, etc.
25 c.c. for the determination of titanium oxide.
50 to 100 c.c. for the determination of ferric oxide.

To 50 c.c. of the main solution in a beaker, add a few c.c. of concentrated nitric acid, and boil. Allow to cool somewhat, then add a slight excess of ammonia, and again bring to the boil and filter immediately. The residue is washed three times with hot water containing ammonium nitrate (see p. 340). The filtrate and washings should be caught in a beaker of large capacity. The precipitated oxides are washed back into the beaker in which the precipitation was effected, and dissolved in a little dilute nitric acid and reprecipitated as above. The precipitate is collected on a filter, and the filtrate caught in the beaker containing the filtrate from the first precipitation. It is washed with hot water containing ammonium nitrate until free from lime, and ignited and weighed. The weight × 500 gives the total percentage of mixed oxides.

Calcium Oxide. The filtrate from the mixed oxides is reduced to about 150 c.c. by evaporation. A few c.c. of ammonia is added and then, while boiling, 20 c.c. of a saturated solution of ammonium oxalate is slowly poured in. The boiling is continued until a granular precipitate is formed and the beaker is removed to a cool place for one hour (during this period the ferric oxide and titanium may be

determined). After settling, the contents are filtered and washed three times by decantation with warm water. Any precipitate on the paper is washed back into the beaker and the calcium oxalate dissolved in a little hydrochloric acid. The bulk is diluted somewhat, an excess of ammonia added and the calcium oxalate precipitated as before. After standing, it is filtered through the previous filter and washed well with warm water. The washed precipitate is dried and then ignited over the blast flame to constant weight. It is weighed as lime, CaO.

Magnesium Oxide. This is determined in the usual manner, as described for cement, see p. 341.

Titanium Oxide. To 25 c.c. of the main filtrate from the silica are added 1 c.c. of phosphoric acid, and 5 c.c. of hydrogen peroxide. The liquid is made up to 100 c.c. in a graduated flask, and well mixed. The titanium is determined colorimetrically in a Nessler or other tube, by comparison with a standard solution of titanium sulphate.

Titanium Sulphate Solution. 0·5 g. pure titanium oxide is fused with 10 g. of potassium bisulphate in a platinum dish until solution is complete. It is cooled, dissolved in dilute sulphuric acid and made up to 1 litre.

Ferric Oxide. 50 or 100 c.c. of the main filtrate from the silica is taken and the total ferric iron determined as for limestone (see p. 296).

As an alternative the following procedure may be adopted. Fifty or 100 c.c. of solution is oxidised with a solution of potassium permanganate, a few c.c. of ammonium thiocyanate solution added, and the whole titrated with titanous chloride solution until the blood red colour is completely discharged. Standardise the titanous chloride with 25 c.c. of a solution containing a known amount of ferric alum, the strength of which can be determined once and for all when made up, and from this calculate the quantity of ferric oxide.

Titanous Chloride Solution. 200 c.c. of 15 per cent. solution plus 300 c.c. of concentrated hydrochloric acid is made up to 2250 c.c. with water, and kept in an atmosphere of carbon dioxide.

Ferric Alum. About a 3 per cent. solution will suffice.

Ferrous Oxide. One g. of cement is placed in a conical flask with 75 c.c. of water and a few pieces of marble. Twenty-five c.c. of sulphuric acid is poured in, the flask fitted with a bunsen valve and the contents boiled for at least thirty minutes. Cool and titrate with standard potassium permanganate of such a strength that 1 c.c. equals 0·005 g. FeO.

The iron existing in the ferrous state should be deducted from the total iron to enable the iron in the ferric state to be computed. The total iron (computed as ferric oxide) should be deducted from the mixed oxides to arrive at the alumina value.

Insoluble Matter, Sulphuric Anhydride. The determination of these components is carried out exactly as for Portland cement (p. 341).

Total Sulphur. The determination is carried as in the case of limestone (see p. 296).

Physical Tests

The physical testing of ciment fondu is conducted exactly as for Portland cement. Standard specifications for this class of material have not yet been published. It complies with the Portland cement specification for soundness and setting time.

A good quality aluminous cement should give figures for the various tests, not less than those indicated below.

Setting Time. Initial Set—about three hours. Final Set—not less than two hours after the initial set.

Expansion. Zero.

Compressive Strength. Carried out on 3 : 1 sand cement mortars—

At 1 day, 5000 lb. per sq. in.
„ 3 days, 6000 „ „
„ 7 „ not less than the value at 3 days.

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DRINKING WATER AND WATER SUPPLIES

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CHEMICALLY pure water does not occur in nature: all natural waters contain varying amounts of salts, etc., in solution. Glacier water is usually the purest form found; rain water is next in purity, but almost always contains, in addition to dissolved gases (nitrogen, oxygen, and carbon dioxide), ammonia (1 to 5 mg. per litre), and traces of nitrous and nitric acids. Furthermore, rain carries down dust particles, from which it extracts minute amounts of mineral constituents such as sodium chloride. Considerable quantities of inorganic constituents, especially sulphuric acid, are found in rain water collected in the neighbourhood of manufacturing towns; micro-organisms and their spores are also always present.[1]

Rain, after falling, sinks into the ground to depths which vary with the nature of the latter, and reappears at the surface as spring water. Below the surface the water comes into intimate contact with mineral substances, varying proportions of which are dissolved. Though the earth's crust is mainly composed of substances almost insoluble in pure water, many such compounds are dissolved because water which has penetrated the ground is charged with carbon dioxide derived from the air in the soil. All spring water consequently contains calcium and magnesium salts, which determine its hardness. Calcium and magnesium are mainly present as bicarbonates in natural waters and only in smaller amounts as sulphates; small amounts of sodium and potassium salts, sulphates, chlorides, and silicates are similarly dissolved. Traces of carbon compounds, the nature of which is unknown, are also present in spring water, though the quantity of organic matter in pure, natural water is very small compared with that of the mineral constituents. Well water is derived from an artificially opened spring fed by ground water, and therefore contains the same constituents as spring water. Some spring waters are characterised by containing larger amounts of dissolved substances, or by having a

[1] See Agnus Smith, *Air and Rain*, *Reports by British Air Pollution Committee*, *Manchester Air Pollution Advisory Board*, *Mellon Institute* (*Pittsburg*) *Reports*, etc.

higher temperature than those ordinarily found; they are then known as natural mineral waters.

After reaching the surface spring water continues its course as brook and river. Meanwhile it comes into contact with the air, which causes decomposition of the bicarbonates, liberation of carbon dioxide, and precipitation of the normal carbonates, which are almost insoluble. River water is therefore softer than spring water. River water also carries along small particles of minerals, such as clay, mica, and quartz, substances of vegetable and animal origin flushed down by rain, and living organisms. These various suspended particles settle to the bottom as the flow becomes more equable. The organic constituents, through the agency of dissolved oxygen, assisted by micro-organisms, are partly mineralised and partly converted into insoluble so-called "humus," which forms part of the deposited mud. This sequence of physical and biochemical processes constitutes what is known as the self-purification of rivers.

This section gives the methods of examination employed for the hygienic valuation of water. Although most of these methods are identical with those used in the testing of water for technical purposes, processes specially suitable for the latter are dealt with, and their importance emphasised, in the section on Feed Water for Boilers (pp. 454-460).

Natural waters may be contaminated by various impurities. The sewers of towns usually empty into rivers, and the water of springs which are situated in the neighbourhood of cesspools or stables may be contaminated by urine and soluble fæcal matter if the earth filtration is insufficient. Apart from the natural repugnance to the use of such water for drinking purposes, it is often directly injurious to health. Experience has shown that such water swarms with micro-organisms, amongst which disease germs may occur. Water is also often contaminated by various industrial works, particularly by factory effluent water (*cf.* "Sewage," p. 461); further, water conveyed by metal pipes may contain heavy metals in solution.

For the determination of the suitability of a water for drinking purposes, the physical and chemical examinations alone suffice only in exceptional cases; microscopic and bacteriological examinations can hardly be dispensed with, and local inspection and geological examination are also of special importance, in order to decide with certainty on the purity or contamination of a water supply (*cf.* "Interpretation of Results," p. 449).

Sampling. The value of a water analysis is largely dependent on correct sampling, as impurities may very easily be introduced from without by the use of imperfectly cleaned collecting vessels, old corks which have been previously used for other purposes, or dirty hands.

For collecting samples only well-cleaned bottles of transparent glass should be used, preferably provided with ground glass stoppers. In taking water from wells provided with pumps, the sample must only be collected after pumping for some time; similarly the water from supply pipes should be first allowed to run for some time, except when contamination by lead is being investigated. Samples are taken from open streams by immersing the collecting vessel in the water; both the surface water, which is often contaminated by dust, etc., and the muddy or sandy bottom, must be excluded. The collecting vessels must in every case be thoroughly rinsed with the water which is to be collected before being finally filled. The taking of the sample is best entrusted to an expert. Two litres usually suffice for a chemical examination. If the dissolved gases are to be determined, or a bacteriological examination to be undertaken, special precautions must be adopted in taking the sample. If the water cannot be examined at once, it must be stored in a cool place, such as a cellar or ice-chest; specially constructed ice-boxes are made for the transportation of water samples for long distances.[1]

THE EXAMINATION OF WATER

Physical Examination

Water for drinking and domestic purposes is examined for temperature, clearness, colour, smell and taste. Determinations of the specific gravity, or of the electrical conductivity, freezing-point, and osmotic pressure (calculated from the latter), such as are now generally made in mineral water investigations, are not usually carried out.

Determination of Temperature

This is carried out with a mercury thermometer graduated in $\frac{1}{10}^{\circ}$, the temperature of the atmosphere being also noted.

When it is impossible to reach the water directly, or to read off the thermometer, a large vessel is filled with the water and its temperature immediately taken. A minimum or maximum thermometer may also be used with advantage, according as to whether the temperature of the water or the atmosphere is the lower.

Clearness, Colour, Smell and Taste

Clearness and Colour. The clearness and colour of water are determined by pouring a sample into cylinders of colourless glass, 20 to 30 cm. high and about 4 cm. wide, placed on white paper. Absolutely colourless and clear water is kept for comparison. The shade and

[1] For details regarding the taking of samples of water, cf. *The Examination of Waters and Water Supplies*, Thresh and Beale, 1925, p. 248.

possible turbidity of the liquid are observed by looking into the cylinders from above.

A simple form of tintometer has been described by T. W. Burgess,[1] which is useful when a large number of samples of water of similar origin have to be compared. It consists essentially of two tubes, each 2 feet long, one of which is filled with distilled water, and the other with the water under observation. The light passing through these is reflected upwards through two short cylinders, and the colour of the water matched with a standard coloured solution contained in the cylinder above the distilled water tube. The standard solution is made by dissolving 1 g. of crystallised cobalt sulphate and 0·05 g. of potassium bichromate in 1000 c.c. of water.

Humus substances impart to the water a yellowish or yellow-brownish shade, which does not disappear on standing for some time, whereas turbidity caused by suspended impurities disappears either completely or partially on settling. Clay imparts a yellowish or greenish coloration, ferric hydroxide, precipitated by the air, a reddish-brown, calcium carbonate a white, and metallic sulphides, such as iron or lead sulphide, a black colour. Further knowledge of the quantity and character of the suspended matter may be obtained by microscopic examination, and also by filtration and subsequent examination of the residue by drying, weighing and ignition. Very finely suspended matter may sometimes pass through good filter papers. The chemical examination of water should usually be preceded by thorough filtration if it is not quite clear.

In the Standard Methods of Water Analysis,[2] published by the American Public Health Association, the turbidity standard adopted by the United States Geological Survey is recommended. This standard is represented by "a water which contains 100 parts of silica per million in such a state of fineness, that a bright platinum wire, 1 mm. in diameter, can just be seen when the centre of the wire is 100 mm. below the surface of the water, and the eye of the observer is 1·2 m. above the wire, the observation being made in the middle of the day, in the open air, but not in sunlight, and in a vessel so large that the sides do not shut out the light, so as to influence the results. The turbidity of such water is arbitrarily fixed at 100." Details as to the preparation of the standard silica, and the manner of making the comparisons, are given in the volume referred to.

Smell. To determine whether a water contains odorous substances, it is warmed to 40° to 50° in a large flask half filled. Any smell becomes noticeable on shaking the water round in the flask.

[1] *Analyst*, 1902, 27, 295.

[2] *Standard Methods for the Examination oj Water and Sewage.* Fifth Edition, American Public Health Association, New York, N.Y., 1923.

Taste. To test for taste the water is warmed to 15° to 20°. Contamination by iron salts, coal-gas, and by products of mould-formation and decay, also by large quantities of common salt, can then be easily detected.

Chemical Examination

The chemical examination of water may be more or less extensive. Determinations of the residue on evaporation, degree of hardness, reducing power, chlorine and albuminoid ammonia, together with qualitative tests for ammonia, sulphuric acid and nitrous acid, are often sufficient, at least for hygienic purposes. A complete analysis is, however, fairly often required, while in some cases the determination of particular constituents, such as magnesia, iron, or lead, is the main essential.

The results of the chemical examination of water are most conveniently expressed in parts per 100,000.

Nitrogen compounds are best expressed in terms of nitrogen to facilitate comparison; thus the terms ammoniacal nitrogen, albuminoid nitrogen, are preferable to free and saline ammonia and albuminoid ammonia, and they can be readily compared with nitrous and nitric nitrogen when progressive change in a sample, either spontaneous or due to special methods of purification, is under observation.

The mineral constituents of a water, according to Thresh,[1] are most usefully expressed in terms of the actual salts assumed to be present, having regard to their relative solubility.

Residue on Evaporation

The residue on evaporation contains all the inorganic and organic substances which were dissolved in the water, with the exception of those compounds which are volatile at relatively low temperatures. For the quantitative determination, 100 c.c. of water is evaporated carefully on the water-bath in a tared platinum or glass dish. To prevent dust particles from falling into the evaporating water, an inverted funnel is fixed above the dish at a suitable height. After complete evaporation, the dish is removed from the water-bath and its outer surface cleaned with a soft, clean cloth; it is then dried in an air-oven for three hours at 100°, placed in a desiccator, allowed to cool and weighed. The first weighing is often somewhat too high, as it always takes some time, and the residue is often hygroscopic. The drying and weighing are therefore repeated until a constant weight is obtained. The final weight is then multiplied by the necessary factor in order to express the weight of the residue in mg. per litre.

[1] Thresh and Beale, *loc. cit.*, p. 349.

To obtain comparable results it is important always to dry the residue at the same temperature. Sell[1] has shown that slightly different values are obtained if the drying is carried out at 100°, 140°, and 180°. The residue dried at 100° sometimes retains considerable quantities of water of crystallisation and hygroscopic moisture, as various inorganic salts, *e.g.* gypsum, magnesium sulphate, and especially calcium and magnesium chlorides, only lose all their water of crystallisation at higher temperatures, and mineral and organic compounds, precipitated in the amorphous state, sometimes retain hygroscopic moisture at 100°. In presence of considerable quantities of the above-mentioned salts, a more accurate result is therefore obtained if the temperature is raised to 140°, or better still to 180°. On the other hand, some substances present in the residue suffer partial decomposition at these temperatures.

To gauge the amount of organic matter present, the platinum dish containing the residue is more strongly heated over a naked flame. If the amount of organic matter is small, the residue acquires a faint yellow colour; if it is large in amount, the residue becomes brown or black. If the organic matter is mainly of vegetable origin, only a faint, non-characteristic smell is noticeable on decomposition, whereas nitrogenous organic matter, if present in considerable quantity, imparts a smell of singed horn to the fumes.

Loss on Ignition.—The quantitative determination of the "loss on ignition" is therefore of little value. In any event it should obviously not all be recorded as "organic matter."

In order to avoid the necessity for a large and expensive platinum dish, the water to be evaporated should be added in small successive portions as the evaporation proceeds. By using an inverted flask provided with an inlet and outlet tube, the former controlled by a pinchcock, the water can be automatically added to the dish drop by drop and so large quantities rapidly evaporated in a small dish.

Reaction and Hydrogen Ion Concentration

The following section is based on the account of the subject by Thresh and Beale (*loc. cit.*, p. 199), who quote from S. W. Cole's *Practical Physiological Chemistry*, where, as these authors rightly state, one of the simplest explanations is to be found which, somewhat abridged, reads as follows:—

"The only satisfactory method of expressing the reaction of a liquid is in the terms of the concentration of hydrogen ions per litre, $[H^{\cdot}]$, of the fluid. A neutral solution is one in which $[H^{\cdot}]$ at 21° = 10^{-7}. An 'acid' solution is one in which $[H^{\cdot}]$ at 21° is greater than 10^{-7}. An 'alkaline' solution is one in which $[H^{\cdot}]$ at 21° is less than 10^{-7}.

[1] *Mitteilungen d. k. Gesundheitamtes*, I., 1881.

"This method of expressing the hydrogen ion concentration is not convenient. It is preferable to adopt the notation of Sorenson, who introduced the symbol *p*H to denote the hydrogen ion exponent. *p*H is the logarithm of [H] to the base 10, the negative sign being omitted. So it will be observed that *p*H decreases as the acidity increases, and *p*H increases as the liquid becomes more alkaline, but the relation is not linear.

"It is important to note that the *p*H of a solution cannot be determined by the ordinary methods of titration. Titration gives an index of the *capacity* of a solution to neutralise acids or alkalies; it does not give us information concerning the *potential* of the hydrogen ion, *i.e.* the *p*H.

"To determine the value of *p*H directly and accurately expensive and intricate electrical apparatus is required, but values sufficiently near for most purposes can be obtained by the use of 'indicators' which vary in colour with the *p*H of the solution, within a range peculiar to each, thus[1]:—

		*p*H range.
No. 1.	Methyl orange	2·9 to 4
,, 2.	Methyl red	4·2 ,, 6·3
,, 3.	Brom-thymol blue	6 ,, 7·6
,, 4.	Cresol red	7·2 ,, 8·8
,, 5.	Phenolphthalein	8·3 ,, 10
,, 6.	Thymol violet	9 ,, 12
,, 7.	Brilliant Cresyl blue	12 ,, 12·4

"The indicators should be of such a strength that 0·1 c.c. added to 10 c.c. of the water suffices. Standard sealed tubes containing solutions of defined *p*H coloured with appropriate indicators are now supplied by leading manufacturers of laboratory equipment, together with a simple 'comparator' stand to facilitate colour matching."[2]

The determination of *p*H value has been found of considerable service in obtaining the optimum conditions for clarifying water or sewage by the addition of "alumino-ferric," the observations being carried out under a microscope provided with an ultra condenser which renders visible fine differences in the character of the "floc."

Alkalinity

Recently collected spring or well water almost always shows a weakly acid reaction, due to the presence of free carbonic acid. Such water remains colourless on addition of a few drops of alcoholic phenolphthalein solution and a drop of lime water. If methyl orange is used as an indicator, most natural waters are apparently alkaline, and it is

[1] Thresh and Beale, *loc, cit.*, p. 266.

[2] An outfit of this description is listed by Messrs Baird & Tatlock, London.

necessary to add a certain amount of hydrochloric acid in order to obtain a definite acid reaction; when this point is reached, all bicarbonates present are just converted into chlorides. If an indicator is used which is sensitive to free carbonic acid, such as phenolphthalein, alizarin, or litmus, this point can only be obtained by vigorously boiling the water during the addition of the hydrochloric acid, and thus driving out the liberated carbon dioxide. This must be borne in mind when defining the alkalinity of natural waters.

Winkler[1] suggests the addition of two drops of a 10 per cent. solution of copper sulphate to 100 c.c. of water, when if no active carbonic acid is present the solution will become turbid in a few minutes, owing to separation of copper carbonate, whereas in presence of active carbonic acid the solution remains clear for at least ten minutes, the copper bicarbonate formed remaining dissolved. On shaking, the carbonic acid escapes and the solution becomes turbid.

According to Lunge[2] the alkalinity is more easily determined by using methyl orange as indicator, as it is then unnecessary to boil, and the use of glass vessels is permissible.

Two to three drops of aqueous methyl orange solution (1 to 1000) are added to 100 c.c. of the water, which is then titrated with $N/10$ hydrochloric acid until the colour becomes reddish.

In the Standard Methods of Water Analysis, erythrosine is recommended in preference to methyl orange for waters containing aluminium or iron sulphates (*cf.* also Section on Feed Water for Boilers, p. 454).

As determinations of alkalinity are easily carried out on the spot, they are particularly suitable in continuous investigations, in order to observe whether the composition of a water undergoes change. Also, the temporary hardness of a water (p. 395) and the half combined and totally combined carbon dioxide (p. 410) can easily be calculated from the alkalinity.

Acidity

For peaty waters, which are very generally acid, Houston[3] recommends lacmoid as a preliminary indicator; the merest trace of acid suffices to change the purplish-blue colour to a red colour.

The solution is best made by dissolving 0·2 g. of lacmoid in 100 c.c. of dilute alcohol (10 per cent.). A few drops added to 10 c.c. of the sample of water, contained in a sample tube, at once reveals the presence of the smallest trace of acid.

[1] L. W. Winkler, *Z. angew. Chem.*, 1915, **28**, 376.

[2] *Die Wasserversorgung von Zürich*, 1885, p. 104.

[3] *Thirteenth Annual Report of the Local Government Board*, 1900-1. Supplement in continuation of the Report of the Medical Officer for 1900-1, "On Lead-poisoning and Water Supplies," p. 67.

Moorland waters which give a neutral reaction with this indicator do not dissolve lead to an appreciable extent. Conversely, whenever a peaty water gives an acid reaction with lacmoid it will also dissolve lead.

If a water is found to give an acid reaction with lacmoid, the amount of the acidity is determined by titrating a definite quantity of the water with a decinormal solution of sodium carbonate (5·3 g. Na_2CO_3 per litre). Phenolphthalein (0·5 g. in 100 c.c. of 50 per cent. alcohol) is used as indicator, as although open to some objections, it is found that comparable results are obtained. The results are expressed as acidity, in terms of c.c. of $N/10$ Na_2CO_3 required to neutralise 100 c.c. of the water.

Hardness

English degrees of hardness (Clark's scale) are equivalent to grains of calcium carbonate per imperial gallon of 70,000 grains; multiplied by 1·43 they give parts per 100,000.

In Germany, degrees of hardness indicate the number of parts by weight of calcium *oxide* in 100,000 parts by weight of water, any magnesium compounds present being taken into account as equivalent quantities of calcium oxide. Thus, if a water is said to have a hardness of 10° it is concluded that in 100,000 parts by weight it contains calcium and magnesium as bicarbonates, sulphates, nitrates, and chlorides equivalent in amount to 10 parts by weight of calcium oxide.

In France, degrees of hardness indicate parts by weight of calcium carbonate in 100,000 parts of water.

Accordingly, 1 English degree of hardness = 0·8 German degree and = 1·432 French degrees.

A water of less than 5 English degrees of hardness is considered soft, of between 5° and 15° moderately hard, and of over 15° as hard.

For the accurate determination of the hardness of a water, the content of calcium and of magnesium is estimated gravimetrically (*cf.* p. 457). Each centigramme of calcium oxide found in 1 litre of water corresponds to 1 part per 100,000; the number of centigrammes of magnesium oxide found per litre multiplied by 1·4 gives its equivalent in calcium oxide. The total hardness is the sum of the hardness due to calcium and magnesium oxides.

Hardness can also be satisfactorily determined by alkalimetry. In Wartha's form of this method[1] the alkalinity of the water is first determined, with alizarin as indicator. This indicator, which on account of its sensitiveness to carbonic acid necessitates titration in

[1] *Cf.* J. Pfeifer, *Z. angew. Chem.*, 1902, **15**, 198: also, H. R. Procter, *J. Soc. Chem. Ind.*, 1904, **23**, 8.

boiling solution, is added to 100 c.c. of the sample and titrated, boiling with $N/10$ hydrochloric acid until the violet colour changes to a clear yellow, which persists on continued boiling. The neutralised water is then treated with an excess of a solution consisting of equal parts of $N/10$ sodium hydroxide and $N/10$ sodium carbonate solutions, boiled for some minutes, cooled, diluted to 200 c.c., filtered, and the excess of alkali determined in 100 c.c. of the filtrate by titration with $N/10$ hydrochloric acid, methyl orange being used as indicator. The number of c.c. of $N/10$ alkali used, multiplied by 3·5, gives the total hardness in English degrees.

A simpler plan in employing this method is to use only one indicator, namely, methyl orange. After determining the alkalinity at the ordinary temperature, the liquid is heated to boiling, $N/10$ sodium hydroxide and carbonate solution added in excess, and the estimation continued as above.

Mohr, and subsequently Hehner, recommend titration with $N/50$ sodium carbonate and $N/50$ sulphuric acid; lacmoid, according to Sutton,[1] being the best indicator. The temporary hardness is obtained by heating 100 c.c. of the water to boiling, and adding the standard acid cautiously in presence of the indicator till the change of colour occurs. The number of c.c. of acid used represent the number of Clark's degrees of temporary hardness per 100,000 parts of water. The permanent hardness is ascertained by taking 100 c.c. of the water, and adding to it a rather large measured excess of the standard sodium carbonate. The whole is then evaporated in a platinum dish to dryness, the soluble portion extracted with small quantities of distilled water, filtered through a very small filter paper, and the excess of sodium carbonate determined in the filtrate by titration with the standard acid: the volume of sodium carbonate solution decomposed represents the permanent hardness.

Clark's Soap Test.—For many technical and most hygienic analyses of water an approximate determination of the hardness is sufficient, and is usually carried out by means of a standard soap solution. Of the methods on this basis, that of Clark[2] is the best known and most widely adopted, although, as Lunge has pointed out, it frequently gives wrong results, and also takes longer to carry out than the more exact methods described above.

The following description of the method is taken from the American Standard Methods of Water Analysis.[3]

Reagents: 1. *Standard Calcium Chloride Solution.* Dissolve 0·2 g. of pure calcite (calcium carbonate) in a little dilute hydrochloric acid, being careful to avoid loss of solution by spattering. Evaporate the

[1] *Volumetric Analysis*, 11th edition, 1924, p. 74.
[2] *Jahresber. f. Chemie*, 1850, p. 608. [3] *Loc. cit.*, p. 28.

solution to dryness several times with distilled water to expel excess of acid. Dissolve the residue in distilled water and dilute the solution to 1 litre. One c.c. of this dilution is equivalent to 0·2 mg. of calcium carbonate.

2. *Standard Soap Solution.* Dissolve 100 g. of dry white Castile soap in 1 litre of 80 per cent. alcohol, and allow this solution to stand several days before standardising. Pure potassium oleate made from lead plaster and potassium carbonate may be used in place of Castile soap.

First Method of Standardisation. Dilute 20 c.c. of the calcium chloride solution in a 250 c.c. glass-stoppered bottle to 50 c.c. with distilled water which has been recently boiled and cooled. Add soap solution from a burette, 0·2 or 0·3 c.c. at a time, shaking the bottle vigorously after each addition until a lather remains unbroken for five minutes over the entire surface of the water while the bottle lies on its side. Then adjust the strength of the stock solution with 70 per cent. alcohol so that the resulting diluted soap solution will give a permanent lather when 6·40 c.c. of it is properly added to 20 c.c. of standard calcium chloride solution diluted to 50 c.c. Usually 75 to 100 c.c. of the stock soap solution is required to make 1 litre of the standard soap solution. The quantity of calcium carbonate equivalent to each c.c. of the standard soap solution consumed in the titration is indicated below:—

Total Hardness in parts per million of $CaCO_3$ for each 0.1 c.c. of Soap Solution when 50 c.c. of the Sample is titrated

c.c. of Soap Solution.	0·0 c.c.	0·1 c.c.	0·2 c.c.	0·3 c.c.	0·4 c.c.	0·5 c.c.	0·6 c.c.	0·7 c.c.	0 8 c.e.	0·9 c.c.
0·0	...	...	...	...	...	...	...	0·0	1·6	3·2
1·0	4·8	6·3	7·9	9·5	11·1	12·7	14·3	15·6	16·9	18·2
2·0	19·5	20·8	22·1	23·4	24·7	26·0	27·3	28·6	29·9	31·2
3·0	32·5	33·8	35·1	36·4	37·7	38·0	40·3	41·6	42·9	44·3
4·0	45·7	47·1	48·6	50·0	51·4	52·9	54·3	55·7	57·1	58·6
5·0	60·0	61·4	62·9	64·3	65·7	67·1	68·6	70·0	71·4	72·9
6·0	74·3	75·7	77·1	78·6	80·0	81·4	82·9	84·3	85·7	87·1
7·0	88·6	90·0	91·4	92·9	94·3	95·7	97·1	98·6	100·0	101·5

This table does not provide for the use of so large volume of soap solution for a single determination as former ones because the end-point becomes somewhat obscured in the presence of magnesium if more than 7 c.c. is used.

Second Method of Standardisation. Dilute 100 c.c. of the stock soap solution to 1 litre with 70 per cent. alcohol. This dilute solution should be of such a strength that approximately 6·4 c.c. of it will give a permanent lather when 20 c.c. of standard calcium chloride solution diluted to 50 c.c. with distilled water is titrated with it.

Determine the amount of soap solution required to give a permanent lather with 50 c.c. of distilled water and with 5, 10, 15 and 20 c.c. of standard calcium chloride solution diluted to 50 c.c. with distilled water. Finally, plot on graph paper a curve showing the relation of various quantities of soap solution to corresponding quantities of standard calcium carbonate solution and therefore to parts per million of hardness.

The hardness of a sample of water is determined as follows:—

Measure 50 c.c. of the water into a 250 c.c. bottle and add to it soap solution in small quantities in precisely the same manner as described for the standardisation of the soap solution. From the number of c.c. of soap solution used obtain from table above or from the plotted curve the total hardness of the water in parts per million of calcium carbonate.

To avoid mistaking the false or magnesium end-point for the true one when adding the soap solution to waters containing magnesium salts, read the burette after the titration is apparently finished, and add about 0·5 c.c. more of soap solution. If the end-point was due to magnesium the lather will disappear. Soap solution must then be added until the true end-point is reached. Usually the false lather persists for less than five minutes.

If more than 7 c.c. of soap solution is required for 50 c.c. of the water, take less of the sample and dilute it to 50 c.c. with distilled water which has been recently boiled and cooled. This step reduces somewhat the disturbing influence of magnesium which consumes more soap than an equivalent weight of calcium.

At best the soap method is not a precise test on account of the different relative amounts of calcium and magnesium in different waters. For hard waters, especially in connection with processes for purification and softening, it is advised that this method be not exclusively used. If the same water is frequently analysed it may be of assistance to standardise the soap solution against a mixture of calcium and magnesium salts, the relative proportions of which approximate those found in the water.

The strength of the soap solution should be determined from time to time, to make sure that it has not materially changed.

A method similar to that of Clark, which allows of the rapid estimation both of the total hardness and of that due to calcium and to magnesium salts individually, has been described by L. W. Winkler.[1]

The above methods give the *total hardness* of the water. On boiling, the greater part of the bicarbonates of calcium and magnesium contained in the water are precipitated as carbonates, whilst the

[1] *Z. anal. Chem.*, 1901, 40, 82; *Z. angew. Chem.*, 1903, 16, 200.

sulphates, nitrates and chlorides remain in solution. The water therefore becomes softer on boiling, and the hardness of the boiled water, after dilution to its original volume with distilled water, is called the *permanent hardness.* The difference between the total hardness and the permanent hardness is known as the *temporary hardness.* The last corresponds approximately to the originally dissolved bicarbonates of calcium and magnesium.

To determine the permanent hardness by Clark's method, the water to be examined is boiled for some time, brought to its original volume, filtered and the hardness of the filtrate determined. The value for the permanent hardness thus obtained is, however, an empirical figure, as the decomposition of the bicarbonates is not complete. The actual amount of bicarbonate present is more simply arrived at by calculating the temporary hardness from the alkalinity of the water (1 c.c. of $N/10$ hydrochloric acid per 100 c.c. water being equal to 3·5 English degrees), and subtracting this from the total hardness.[1]

A useful and accurate method for determining the hardness due to magnesium and calcium salts respectively has been published by Kay and Newlands.[2] It depends on the fact that magnesium carbonate is soluble in excess of hot ammonium carbonate solution, whereas calcium carbonate is practically insoluble. The procedure is as follows :—

Measure 100 c.c. of the water into a platinum basin, and 10 c.c. of a 2 per cent. solution of ammonium carbonate (2 g. of the solid and 1 c.c. of concentrated ammonia in 100 c.c.) and evaporate to dryness on the steam-bath. Pour 15 c.c. of the same ammonium carbonate solution into the basin, bring the liquid into contact with the whole of the residue, and allow the basin to remain on the steam bath for about two minutes. Filter through a 5½ cm. paper, retaining the undissolved carbonate as far as possible in the basin. Repeat the extraction twice, using about 10 c.c. of ammonium carbonate each time. Rinse the platinum basin four times with 90 per cent. alcohol, and wash the filter with the same alcohol until the filtrate is free from alkali. (Litmus paper is too insensitive for this purpose and absence of alkali may be ascertained by allowing about 5 c.c. of the filtrate to drop into a little water containing methyl red and a trace of 0·02 N acid.) Dissolve the calcium carbonate, which now alone remains in the basin and on the filter, in a measured volume of 0·1 N hydrochloric acid (usually 5 to 10 c.c.) and titrate the excess of acid with 0·02 N baryta solution.

[1] *Cf.* J. Pfeifer, G. Lunge, and also H. R. Procter, *loc. cit.*

[2] "Determination of Calcium and Magnesium in Waters," by Sydney A. Kay, and Susan H. Newlands, *J. Soc. Chem. Ind.*, 1916, **35**, 445.

The amount of calcium in the water, expressed in degrees of hardness, is then calculated, and the difference between the total hardness and that due to calcium gives the hardness, in degrees, due to magnesium.

In mineral waters, and boiler-feed waters which have been softened with an excessive quantity of sodium carbonate, the temporary hardness calculated from the alkalinity may be apparently greater than the total hardness; this water has of course no permanent hardness, and contains sodium carbonate in excess. This has also been found to occur in numerous samples of water obtained from the chalk below the London clay,[1] and in Yorkshire waters.[2]

Reducing Power or "Oxygen Absorption"

In the purer natural waters the quantity of organic matter present is usually only minute, and consists essentially of products of decomposition of vegetable remains; these contain, as a rule, little nitrogen, and are known as humus substances. On the other hand, highly nitrogenous decomposition products of animal refuse and remains of metabolic products of the animal organism also occur, more particularly in waters which are exposed to surface impurities, or which come into contact with polluted ground. The organic compounds of this character vary greatly in properties. Some are easily oxidised and easily decomposed, whilst others are stable and are oxidised only with difficulty; some are volatile with water vapour at relatively low temperatures, others remain behind when the water is evaporated; finally, some are basic, whilst others are acidic in character. Their importance, from a hygienic standpoint, also varies greatly. While the organic substances derived from vegetable remains may in general be considered as hygienically indifferent, the presence of nitrogenous decomposition products from animal organisms makes a water highly suspicious.

The quantitative estimation of the individual organic compounds in water offers great and, in part, insuperable difficulties, both on account of their variety and also because their composition is in many cases still unknown. The determination is accordingly at present restricted to ascertaining whether a water contains serious quantities of organic impurities, and whether these are mainly of vegetable or of animal origin. From a purely hygienic standpoint, the second question is the more important.

As it is impossible to determine the quantity of organic compounds in water directly, an indirect method is adopted, which consists in

[1] W. W. Fisher, *Analyst*, 1901, **26**, 202.
[2] H. R. Procter, *J. Soc. Chem. Ind.*, 1904, **23**, 8.

estimating their total reducing power; an approximate valuation of the content of organic matter is thus obtained.

An approximate differentiation of the nature of the organic impurities is effected by separating and estimating the nitrogen in the form of the so-called "Albuminoid" or "Proteid Nitrogen."

The determination based on the oxidation of the organic matter will be considered first; the determination of albuminoid and of proteid nitrogen is described later (p. 416).

The reducing power of a natural water is determined by means of potassium permanganate. In the past considerable discussion has taken place as to whether this oxidation should be carried out in acid or alkaline solution, at boiling temperature or at atmospheric temperature. The method in any event is empirical and mainly useful for rapid comparative purposes.

It will generally therefore be found most convenient to allow the permanganate to act in acid solution for a definite time at atmospheric temperature. This method is most in use in England, boiling in acid solution is practised in the United States and boiling in alkaline solution in Germany.

It is usual to express the amount of organic impurity in water in terms of the amount of oxygen necessary for its oxidation, calculated on 100,000 parts of water.

The following details for the oxidation in acid solution are based on the American Standard Methods:—

Reagents: 1. *Dilute Sulphuric Acid.* Dilute one part of concentrated sulphuric acid with three parts of distilled water and free the solution from oxidisable matter by adding potassium permanganate until a faint pink colour persists after the solution has stood several hours.

2. *Standard Ammonium Oxalate.* Dissolve 0·888 g. of the pure salt in 1 litre of distilled water. One c.c. is equivalent to 0·1 mg. of oxygen. An equivalent quantity of oxalic acid or sodium oxalate may be used.

3. *Standard Potassium Permanganate.* Dissolve 0·4 g. of the crystallised salt in 1 litre of distilled water, and digest for thirty minutes. Add 10 c.c. of the dilute sulphuric acid and 10 c.c. of this solution of potassium permanganate to 100 c.c. of distilled water and digest for thirty minutes. Add 10 c.c. of the ammonium oxalate solution, and then add potassium permanganate till a pink coloration appears. This destroys the oxygen-consuming capacity of the water used. Now add another 10 c.c. of ammonium oxalate solution and titrate with potassium permanganate. Adjust the potassium permanganate solution so that 1 c.c. is equivalent to 1 c.c. of ammonium oxalate solution or 0·1 mg. of available oxygen.

4. *Potassium Iodide Solution.* Ten per cent. solution free from iodate.

5. *Sodium Thiosulphate Solution.* Dissolve 1·0 g. of the pure crystallised salt in 1 litre of distilled water. Standardise against a potassium permanganate solution which has been standardised against an ammonium oxalate solution. As this solution does not keep well, determine its actual strength at frequent intervals.

6. *Starch Indicator.* Mix a small amount of clean starch with cold water until it becomes a thin paste, and stir this into 150 to 200 times its weight of boiling water. Boil for a few minutes, then sterilise. The solution may be preserved by adding a few drops of chloroform.

Method of Determination. The quantities of water and of reagent used must be determined to some extent by the character and amount of oxidisable matter present. The important condition to maintain is that the permanganate shall always be present in excess, and in the case of high grade waters that enough of the sample be taken to obtain definite measurable results.

For a good average water 250 c.c. of the sample may be taken and 10 c.c. of sulphuric acid and afterwards 25 c.c. of permanganate.

Clean conical flasks are convenient for this purpose, and the samples with the added sulphuric acid and permanganate are allowed to stand for four hours, being protected from dust, etc., by small caps of filter paper over the mouth of each flask. A blank test should be made with an equal quantity of pure distilled water. If the permanganate in any sample shows signs of becoming appreciably decolorised during the course of the four hours, a further 25 c.c. should be added to maintain an excess.

At the end of the period of standing, add 0·5 c.c. of potassium iodide solution (or better, a crystal of the pure salt) to discharge the pink colour, mix and titrate the liberated iodine with thiosulphate until the yellow colour is nearly destroyed; then add a few drops of starch solution and continue the titration until the blue colour is just discharged.

When unoxidised mineral substances, such as ferrous sulphate, sulphides, nitrites, etc., are present in the sample, corrections should be applied as accurately as possible, by methods suitable for the samples analysed. Direct titration of the acidified sample in the cold, using a three-minute period of digestion, serves this purpose quite well for polluted surface waters and fairly well for purified sewage effluents. In all samples containing both unoxidised mineral compounds and gaseous organic substances, the latter should be driven off by heat and the sample allowed to cool before applying this test for the correction factor.

Where such corrections are necessary the fact should be stated, with the amount of the correction.

Silica

Silica is usually present in natural waters only in very small quantities. It is of no importance from a hygienic standpoint, but the presence of appreciable quantities of silica becomes a consideration in the analysis of water for technical purposes, as it is one of the substances which give rise to boiler incrustations.

To determine silicic acid, from 500 to 1000 c.c. of the water is acidified with hydrochloric acid and evaporated to dryness. The residue is moistened several times with hydrochloric acid, completely evaporated after each addition, and then dissolved in hot water with addition of hydrochloric acid. The silicic acid, which forms flocculent particles, is collected on a small filter, washed successively with dilute hydrochloric acid and with hot water, ignited and weighed as silica. The filtrate may be used for the gravimetric estimation of sulphuric acid, or of calcium and magnesium.

If the sample contains much calcium sulphate, it may be retained by the precipitated silica. The impure silica is then fused with ten times its weight of fusion mixture and the silicic acid again separated.

Sulphuric Acid

For the qualitative detection of sulphuric acid, about 10 c.c. of the water is acidified with hydrochloric acid and a few drops of barium chloride solution added. If the water contains 100 mg. SO_3 per litre, a white powdery precipitate is formed at once; 10 mg. SO_3 per litre give a white turbidity after some minutes; 2 mg. SO_3 per litre give a scarcely perceptible turbidity after standing for a considerable time.

The quantitative, gravimetric estimation of sulphuric acid depends on the same reaction. From 500 to 1000 c.c., or from 200 to 300 c.c., is taken for the estimation, according as to whether the qualitative test gave a turbidity or a considerable precipitate. The sample is acidified with hydrochloric acid and evaporated to dryness on the water-bath; should considerable quantities of nitrates be present a glass dish must be used for this purpose, as platinum is attacked. The residue is moistened with dilute hydrochloric acid, dissolved in about 50 c.c. of hot, distilled water, the silica filtered off and washed with 50 c.c. of hot water, and the filtrate precipitated with barium chloride, after the addition of ammonium chloride solution.

For technical and hygienic purposes an approximate determination of the sulphuric acid is sufficient; this can be quickly carried out colorimetrically. The principle of the method consists in decomposing the dissolved sulphate with excess of barium chromate in hydrochloric acid solution, then neutralising the liquid with sodium hydroxide, filtering, and finally determining the amount of chromic acid in the

filtrate colorimetrically; this is equivalent in quantity to the amount of sulphuric acid originally present.[1]

The barium chromate is prepared by adding an excess of potassium chromate solution to a solution of barium chloride acidified with a few drops of acetic acid. The precipitate is first washed by decantation, then thoroughly on the filter, dried and ground to a powder. The chromate can also be kept under water. Five to 10 drops of the turbid liquid are taken for use after shaking.

To carry out the estimation, 150 to 200 c.c. of the water under examination is poured into a flask and acidified with 5 to 10 drops of fuming hydrochloric acid. 0·1 to 0·2 g. of pure barium chromate is then added, and the solution heated just to boiling, over the free flame. After cooling completely, sodium hydroxide solution is added until the liquid just turns red litmus paper faintly blue; a larger excess of sodium hydroxide is to be avoided. Finally the liquid is vigorously shaken, allowed to stand for a few minutes, and poured through a dry, double filter-paper; the first portions of the filtrate, which are usually turbid, are rejected, and the later, perfectly clear portions used for the determination. One hundred c.c. of the filtrate is poured into a cut-glass bottle, and 100 c.c. of distilled water, to which a few drops of sodium hydroxide solution are added, poured into a similar bottle for comparison. Potassium bichromate solution is then added from a burette to the contents of the second bottle until the colours of the two solutions correspond. The colour comparison may also be carried out in glass cylinders about 20 cm. high and 4 cm. wide. If 0·7 c.c. is deducted from the amount of potassium bichromate solution used, to allow for the amount of dissolved barium chromate, and the remainder multiplied by 10, the weight of SO_3 is obtained in mg. To express the result in terms of SO_4 the result is multiplied by 1·2.

The potassium bichromate solution is prepared by dissolving 1·839 g. of the pure salt in water and making up to 1 litre; each c.c. of this solution represents 0·0001 g. SO_3.

If the water contains considerable quantities of organic matter some of the chromic acid is reduced, and less sulphuric acid found than is actually present. In such cases the organic matter must be destroyed before determining the sulphuric acid. For this purpose a measured quantity of the water, for instance 200 c.c., is treated with 5 to 10 drops of fuming hydrochloric acid and a few c.c. of strong chlorine water; the excess of chlorine is then boiled off, the liquid cooled, diluted to its original volume, and the sulphuric acid then determined as described above.

[1] *Cf.* L. W. Winkler, *Z. anal. Chem.*, 1901, 40, 467; also, Hartleb, *Chem. Centr.*, 1901, II., 320; and Rossi, *ibid.*, 1902, II., 1272.

Chlorine

Combined Chlorine (*Chlorides*). Chlorides are tested for qualitatively by adding a few drops of nitric acid and silver nitrate solution to about 10 c.c. of the sample. The amount of chloride present can be approximately estimated from the intensity of the reaction: 100 mg. of chlorine per litre produce a milky liquid from which silver chloride separates in flocks on shaking; 10 mg. per litre give a strongly opalescent liquid and 1 mg. per litre a very faint opalescence.

The quantitative estimation of chloride may be made either gravimetrically or volumetrically by the usual methods (*cf.* p. 455).

L. W. Winkler[1] has modified Mohr's volumetric method, for the purpose of water analysis, by determining experimentally the amount which must be deducted from the volume of silver nitrate solution used to allow for the volume required for the coloration of the indicator. If a silver nitrate solution is employed, of which 1 c.c. is equivalent to 1 mg. of chlorine, and 1 c.c. of a 1 per cent. potassium chromate solution is used as indicator, and the determinations are carried out with 100 c.c. of water, then the necessary corrections are given by the following table:—

Silver Solution used, in c.c.	Deduction, in c.c.	Silver Solution used, in c.c.	Deduction, in c.c.	Silver Solution used, in c.c.	Deduction, in c.c.	Silver Solution used, in c.c.	Deduction, in c.c.
0·2	−0·20	0·7	−0·38	3·0	−0·46	7·0	−0·54
0·3	−0·25	0·8	−0·39	4·0	−0·48	8·0	−0·56
0·4	−0·30	0·9	−0·40	5·0	−0·50	9·0	−0·58
0·5	−0·33	1·0	−0·41	6·0	−0·52	10·0	−0·60
0·6	−0·36	2·0	−0·44				

In presence of large quantities of organic matter, which, though seldom present in a domestic water supply, may easily occur in a works' supply, a direct titration with silver nitrate is impossible, as the end of the reaction is obscured by the colour of the sample. In such waters the organic matter must be destroyed before titration. To effect this, 200 c.c. of the water is warmed to about 100°, and neutral potassium permanganate solution added until the water is faintly red in colour; it is then boiled for about five minutes, when, if the colour is destroyed, a few more drops of permanganate solution are added. The hot liquid is then treated with a few drops of alcohol to remove the excess of permanganate, allowed to stand for a quarter of an hour, the precipitated manganese compounds filtered off, and the filtrate, after allowing to cool, diluted to 200 c.c.; the solution, which must be neutral, is then divided into two equal portions and titrated.

[1] *Z. anal. Chem.*, 1901, **40**, 596.

The same procedure is adopted if the water contains sulphuretted hydrogen.

In presence of large quantities of organic matter, the chlorides may be determined in the residue on evaporation, after first removing the organic matter by careful ignition. The residue is dissolved in as little cold, distilled water as possible, with addition of a few drops of nitric acid, the liquid filtered, a few crystals of potassium bicarbonate dissolved in it (an excess does not matter) and the chloride titrated in the usual way (*cf.* p. 455).

Free Chlorine and Hypochlorites. From 100 to 500 c.c. of the sample is treated with 1 g. of potassium iodide and 50 per cent. acetic acid, and the liberated iodine titrated with $N/10$ sodium thiosulphate solution; the titration is continued until a pale yellow coloration remains, freshly prepared starch solution is then added and the titration completed. One c.c. $N/10$ sodium thiosulphate solution = 0·003545 g. Cl. Acetic acid is used instead of hydrochloric in the titration, as the results are then unaffected by the presence of chlorates or of iron in the liquid.[1]

The following method is suggested by the American Public Health Association.[2]

In waters which have been treated with calcium hypochlorite or liquid chlorine it is frequently advisable to ascertain the presence or absence of chlorine. As the reagents which have been proposed for its detection are not specific for chlorine but give similar or identical reactions with oxidising agents or reducible substances, care must be exercised in interpreting the results of such tests; nitrites and ferric salts are of common occurrence, and chlorates may also lead to misinterpretation in waters treated with calcium hypochlorite.

Reagents—Tolidine Solution. One g. of *o*-tolidine (diaminodimethyldiphenyl) purified by recrystallisation from alcohol, is dissolved in 1 litre of 10 per cent. hydrochloric acid.

Copper Sulphate Solution. Dissolve 1·5 g. of copper sulphate and 1 c.c. of concentrated sulphuric acid in distilled water and dilute the solution to 100 c.c.

Potassium Bichromate Solution. Dissolve 0·025 g. of potassium bichromate and 0·1 c.c. of concentrated sulphuric acid in distilled water and dilute the solution to 100 c.c.

Procedure. Mix 1 c.c. of the tolidine reagent with 100 c.c. of the sample in a Nessler tube and allow the solution to stand at least five minutes. Small amounts of free chlorine give a yellow and larger amounts an orange colour.

For quantitative determination compare the colour with that of standards in similar tubes prepared from the solutions of copper

[1] Schultz, *Z. angew. Chem.*, 1903, **23**, 833.
[2] *Loc. cit.*, p. 64.

sulphate and potassium bichromate. The amounts of solution for various standards are indicated in the following table:—

Preparation of Permanent Standards for Content of Chlorine

Chlorine. Parts per million.	Solution of Copper Sulphate. c.c.	Solution of Potassium Bichromate. c.c.
0·01	0·0	0·8
0·02	0·0	2·1
0·03	0·0	3·2
0·04	0·0	4·3
0·05	0·4	5·5
0·06	0·8	6·6
0·07	1·2	7·5
0·08	1·5	8·7
0·09	1·7	9·0
0·10	1·8	10·0
0·20	1·9	20·0
0·30	1·9	30·0
0·40	2·0	38·0
0·50	2·0	45·0

Iodine

The occurrence of iodine in combination with albumins in the secretions of the thyroid gland having drawn attention to its great physiological importance, the presence of iodine in drinking waters has become of interest as a possible source of the supply of this element to the system.

To detect iodine in water, and simultaneously to determine its approximate amount, 1000 c.c. of the sample is treated with a few drops of sodium hydroxide solution, evaporated down to about 10 c.c., filtered into a wide test-tube, and the residue washed with about 5 c.c. of water. The combined filtrate and washings are acidified with hydrochloric acid, a drop of potassium nitrite solution added, followed by 5 c.c. of chloroform, and the whole vigorously shaken. Should the water contain 0·1 mg. of iodine, the chloroform is at once coloured pink. To estimate approximately the amount of iodine present, 15 c.c. of distilled water is placed in a second test-tube, 5 c.c. of chloroform, a few drops of hydrochloric acid, and a drop of nitrite solution added, and then a very dilute potassium iodide solution, of which 1 c.c. = 0·1 mg. iodine; the addition of the iodide solution is continued until, on shaking, the chloroform is coloured to the same extent as in the sample under examination.

For the exact determination of small amounts of iodine the method described by Weszelszky[1] may be used.

[1] *Z. anal. Chem.*, 1900, **39**, 85.

Nitric Nitrogen

The most rapid and satisfactory qualitative tests for nitric nitrogen in natural waters are the following:—

The Brucine-Sulphuric Acid Test. About 1 c.c. of the water is added drop by drop to 3 c.c. of concentrated sulphuric acid, and after cooling completely, a few mg. of brucine is added to the solution. From the intensity of the colour one can judge whether much, little, or only traces of nitric acid are present. One hundred mg. of N_2O_5 per litre causes a cherry-red coloration, which soon changes to orange and then to a sulphur-yellow on long standing; 10 mg. per litre gives a rose-red solution, which changes to pale yellow on long standing; and 1 mg. per litre give a pale rose-coloured solution, which becomes almost colourless on standing.

If the brucine is dissolved in the liquid while the latter is still hot, the coloration changes to yellow almost immediately.

The Diphenylamine Test. A solution of 0·05 g. diphenylamine in 10 c.c. sulphuric acid gives a blue coloration with nitrates.[1]

The Sulphuric Acid-Pyrogallol Test. When pyrogallol, sulphuric acid and salt are added to water containing nitrates in solution, a purple colour is produced. This test is described in detail on p. 475.

None of these tests are suitable for exact quantitative determinations, while methods based on the reduction of indigo are also unsatisfactory. The writer's experience in this connection coincides exactly with that of Thresh (*loc. cit.*, p. 293) that the most trustworthy method is reduction by the zinc-copper couple.

Reduction by the Zinc-Copper Couple.[2] The nitrogen present as nitrate is determined by reducing it to ammonia, and estimating the latter by Nesslerising (*cf.* p. 415). The method is simple and gives very accurate results.

As is obvious, any nitrite present will also be reduced; the nitrogen combined as nitrite must therefore be separately estimated and deducted from the nitrogen present as nitrate.

The zinc-copper couple is prepared as follows:—A piece of zinc foil about 15 cm. long by 5 cm. wide is rolled into a cylinder about 1·5 cm. in diameter, then dipped for a moment into strong hydrochloric acid, to clean the surface of the metal, and afterwards well washed in water. The clean cylinder is transferred for a few moments to a 3 per cent. solution of copper sulphate until evenly coated with a black layer of copper. It is then again washed by gently immersing it in clean water so as not to dislodge the film of copper.

Before bringing the sample into contact with the couple, it is

[1] O'Shaughnessy, *J. Soc. Chem. Ind.*, 1912, 31, 96.

[2] Cf. *Sewage Works Analyses*, by G. J. Fowler, pp. 68-70.

advisable first to drive off any free ammonia, if much is present, as otherwise the total amount of ammonia to be determined by Nesslerising may be inconveniently large, and the free ammonia must be deducted from the total ammonia present after reduction. Any error in the determination of free ammonia will therefore affect the nitrate determination.

One hundred c.c. of the water, or less if much nitrate is present, is diluted to 200 c.c. with distilled water free from nitrate and boiled down to about 50 c.c. This residual solution from which the free ammonia has been expelled is poured into a glass cylinder 15 cm. high by 2·5 cm. in diameter, and the zinc-copper couple, prepared as above, added. Thorough contact of the couple and the solution is thus ensured.

On slightly acidifying the solution with dilute acetic acid (1 : 2), an evolution of hydrogen occurs which reduces the nitrate to ammonia. For the reaction to be complete it should be left overnight, and as a further precaution, a known volume of the solution may be tested for nitrites in the morning; if present, it is evident that the reduction to ammonia is incomplete, and must be continued, but this is seldom, if ever, necessary. If the reduction is complete the solution is poured off from the couple into a litre flask, the couple washed free from adhering liquid and the washings added to the contents of the flask. Any free acid still remaining is neutralised with a little powdered sodium carbonate; tap water is then added to make up the volume to about 500 c.c., and the ammonia distilled off and estimated as on p. 415.

From time to time a blank experiment should be made with the reagents used, the whole process being conducted as above, with the exception that distilled water is substituted for the sample. Any ammonia found in the blank experiment must be deducted from the total amount obtained from the sample.

Colorimetric determination with Phenolsulphonic Acid. For clear waters and good sewage effluents, the colorimetric determination with phenolsulphonic acid gives good results, provided certain precautions are taken, particularly the removal of chlorides, if present in appreciable quantity, by silver sulphate. These precautions are embodied in the following description of the process.[1]

Reagents: Phenoldisulphonic Acid. Dissolve 25 g. of pure white phenol in 150 c.c. of pure concentrated sulphuric acid (15 per cent. SO_3), stir well and heat for two hours at about 100°.

Potassium Hydroxide Solution. Prepare an approximately 12 *N* solution, 10 c.c. of which will neutralise about 4 c.c. of the phenoldisulphonic acid.

[1] Cf. *Standard Methods of Water Analysis*, p. 20.

Standard Nitrate Solution. Dissolve 0·72 g. of pure recrystallised potassium nitrate in 1 litre of distilled water. Evaporate cautiously to dryness 10 c.c. of the solution on the water-bath. Moisten the residue quickly and thoroughly with 2 c.c. of phenoldisulphonic acid and dilute to 1 litre. This is the standard solution, 1 c.c. of which equals 0·001 mg. of nitrate nitrogen.

Standard Silver Sulphate Solution. Dissolve 4·4 g. of silver sulphate free from nitrate in 1 litre of water. One c.c. of this solution is equal to 1 mg. of chloride.

Procedure. The alkalinity, chloride and nitrite content and colour of the sample must first be determined. If the sample is highly coloured, decolorise it with freshly precipitated aluminium hydroxide. Measure into an evaporating dish 100 c.c. of the sample, or if nitrate is very high, such volume as will contain about 0·01 mg. of nitrate nitrogen. Add sufficient $N/50$ sulphuric acid nearly to neutralise the alkalinity. Then add sufficient standard silver sulphate to precipitate all but about 0·1 mg. of chloride. The removal of chloride may be omitted if the sample contains less than 30 parts per million of chloride. Heat the mixture to boiling, add a little aluminium hydroxide, stir, filter, and wash with small amounts of hot water. Evaporate the filtrate to dryness, and add 2 c.c. of the phenoldisulphonic acid, rubbing with a glass rod to ensure intimate contact. If the residue becomes packed or appears vitreous because of the presence of much iron, heat the dish on the water-bath for a few minutes. Dilute the mixture with distilled water, and add slowly a strong solution of potassium hydroxide or ammonium hydroxide until the maximum colour is developed. Transfer the solution to a Nessler tube, filtering if necessary. If nitrate is present a yellow colour will be formed. Compare the colour with that of standards made by adding 2 c.c. of strong potassium hydroxide or ammonium hydroxide to various amounts of standard nitrate solution and diluting them to 50 c.c. in Nessler tubes. The following amounts of standard nitrate solution are suggested: 0, 0·5, 1·0, 1·5, 2·0, 4·0, 6·0, 8·0, 10·0, 15·0, 20·0, and 40·0 c.c. These standards may be kept several weeks without deterioration. If 100 c.c. of water is used the number of c.c. of the standard multiplied by 0·01 is equal to parts per million of nitric nitrogen.

Standards that will remain permanent for several years if stored in the dark may be prepared from tripotassium nitrophenoldisulphonate.

If nitrous nitrogen is present in excess of 1 part per million, it should be oxidised by heating the samples a few minutes with a few drops of hydrogen peroxide free from nitrate, repeatedly added, or by adding dilute potassium permanganate in the cold until a faint pink coloration appears; the nitrogen equivalent of the nitrite thus oxidised to nitrate is then subtracted from the final nitrate nitrogen reading.

Nitrous Nitrogen

Nitrous acid is detected qualitatively by adding a few drops of potassium iodide solution and 1 c.c. of starch solution to about 50 c.c. of the water, placed in a cylinder of colourless glass, and then acidifying the liquid with a few drops of dilute sulphuric acid. Iodine is liberated in presence of nitrous acid, and gives a blue coloration, the intensity of which varies according to the amount present. Direct sunlight should be avoided in making the test; the reaction is also only decisive if the blue coloration takes place immediately, or at latest within five minutes. Mistakes are best avoided by carrying out a parallel test with 50 c.c. of pure distilled water. The reaction is delicate; 0·1 mg. of nitrous acid per litre of water gives a distinct blue coloration. With small quantities of nitrous acid the presence of considerable quantities of organic matter may prevent or considerably retard the reaction; it has, however, been shown by Preusse and Tiemann that the reduction of nitrates in presence of sulphuric acid and organic matter, which Kammerer[1] regarded as likely to occur, does not take place. If iron is present in the water it must be removed, as ferric salts liberate iodine from solutions of metallic iodides.

Metaphenylenediamine Test. Tiemann and Preusse have applied the metaphenylenediamine reaction discovered by Griess[2] to the detection and quantitative estimation of nitrous acid in water; triaminoazobenzene (Bismarck brown) is formed. The reaction is extremely sharp; with practice the coloration produced by 0·03 mg. of N_2O_3 per litre can be recognised after an interval of about ten minutes. The reagent is prepared by dissolving 5 g. of metaphenylene-diamine in water, adding dilute sulphuric acid at once until the liquid shows a distinctly acid reaction, and then diluting with distilled water to 1 litre. If the solution is coloured it must be decolorised by warming with ignited charcoal. It can be satisfactorily kept for months in a well-closed vessel.

To detect nitrous acid, 100 c.c. of the water is acidified with 1 c.c. of 30 per cent. sulphuric acid, in a cylinder of colourless glass, and 1 c.c. of the metaphenylenediamine solution added; a yellowish, golden-yellow, or yellowish-brown coloration is produced, according to the amount of nitrous acid present. The presence of organic matter does not affect the reaction. Aqueous solutions of metaphenylenediamine are very sensitive to the action of ferric compounds which colour them more or less yellow, but excess of sulphuric acid makes the diamine solution much more stable in this respect, so that the presence of small quantities of iron compounds does not essentially influence the reaction if the test is carried out as described above.

[1] *Z. anal. Chem.*, 1873, **12**, 377. [2] *Ber.*, 1878, **11**, 624.

α-Naphthylamine and Sulphanilic Acid Test. A subsequent method for detecting nitrous acid, also proposed by Griess,[1] but modified by Ilosvay[2] and by Lunge,[3] depends on the fact that an acetic acid solution of α-naphthylamine and sulphanilic acid gives a distinct red coloration after a short time in presence of extremely small quantities of nitrous acid. Pagnini[4] fixes the dyestuff on wool. F. G. Germuth[5] states that dimethyl-α-naphthylamine is a more sensitive and stable reagent than α-naphthylamine.

The reagent is prepared as follows:[6]—

(1) One g. of sulphanilic acid is dissolved in 14·7 g. of glacial acetic acid and 285 c.c. of water. This is best done by warming the sulphanilic acid with the glacial acetic, to which an equal bulk of water has been added. The remaining water should be added carefully, the mixture being warmed and stirred to keep the sulphanilic acid in solution.

(2) 0·2 g. of α-naphthylamine is dissolved in 14·7 g. of glacial acetic acid and 325 c.c. of water. The naphthylamine is also best dissolved by warming first with the acid, to which about twice its volume of water has been added, and afterwards adding the remainder of the water.

Equal volumes of the two solutions are mixed for use. The greater portion of the solutions should, however, be kept separately, not more than two or three days' supply of the mixture being made up at once, as it tends to turn pink, owing to the development of nitrite in the solution from the air.

To carry out the test, 20 c.c. of the water is mixed with 2 to 3 c.c. of the reagent and warmed to 70°-80°. In presence of 0·001 mg. of nitrous acid per litre, a red coloration is observed within one minute. The test must be performed in filled stoppered vessels, as the nitrous acid present in the air is sufficient to show a reaction, the coloration from which travels down through the liquid from above, if its surface is exposed to the atmosphere for some time. According to observations by Tiemann the presence of nitric acid, ammonia, or of organic matter in the water exerts no appreciable effect on the reaction.

If nitrous acid is present only in traces, its qualitative detection is usually sufficient. The quantitative estimation of minute quantities is effected colorimetrically by the methods of Trommsdorff,[7] Preusse and Tiemann,[8] or Lunge and Lwoff (Vol. I., p. 449); larger amounts of nitrous acid are determined iodometrically as follows:—

One hundred c.c. of the water is poured into a flask of 200 c.c. capacity, acidified with 20 c.c. of 10 per cent. hydrochloric acid, and

[1] *Ber.*, 1879, **12**, 427
[2] *Bull. Soc. Chim.*, 1889 [3], **2**, 317.
[3] *Z. angew. Chem.*, 1889, **2**, 666.
[4] *Chem. Centr.*, 1902, II., 770.
[5] *Ind. Eng. Chem.* (Anal. Ed.), 1929, **1**, 28; cf. *Water Pollution Research*, vol. iii., 1930, p. 156.
[6] *Cf.* Fowler, *Sewage Works Analyses*, p. 64.
[7] *Z. anal. Chem.*, 1869, **8**, 358; 1870, **9**, 168.
[8] *Ber.*, 1878, **11**, 627.

2 to 3 c.c. of starch solution added; about 5 g. of pure potassium hydrogen carbonate, in fair-sized crystals, is then added to the liquid. After gas has been evolved for about one minute, a small crystal (0·1 to 0·2 g.) of potassium iodide is added, and the separated iodine titrated after five minutes, with a very dilute sodium thiosulphate solution, of which 1 c.c. is preferably equivalent to 0·1 mg. N_2O_3. This solution is prepared either by diluting 26·3 c.c. of *N*/10 sodium thiosulphate solution to 1000 c.c., or by dissolving 0·6532 g. of pure $Na_2S_2O_3 . 5H_2O$ in water and making up to 1 litre. The blue coloration of the liquid should not return within ten minutes of the completion of the reaction, otherwise the expulsion of the air or of the nitric oxide was incomplete ($2HI + N_2O_3 = 2NO + I_2 + H_2O$).

If the sample is turbid, or coloured yellow by iron rust, it must first be filtered; it is also advantageous to remove ferrous iron. To remove all the iron with certainty, 1 to 2 c.c. of sodium hydroxide solution, free from nitrite, is added to 250 c.c. of the water, which is then allowed to stand in a completely filled stoppered flask for half a day; the water is then decanted or filtered off from the precipitate and the nitrous acid estimated.

Should the water contain considerable quantities of organic matter, this might combine with part of the liberated iodine, and thus give too low a value for the nitrous acid. To eliminate this source of error, 1 c.c. of iodine solution is added to 100 c.c. of the water under examination and to 100 c.c. of distilled water, and the iodine remaining in each liquid titrated after five minutes; the difference corresponds to the correction to be added. This method can of course be adopted without modification in the case of water clarified by filtration or by sedimentation, but not if it has been clarified with the help of caustic alkali when it is strongly alkaline; in the latter case pure carbon dioxide is first passed through the liquid until it no longer turns phenolphthalein paper red; a large excess of carbon dioxide is to be avoided.

Phosphoric Acid

To test for phosphoric acid qualitatively, from 500 to 1000 c.c. of the water is acidified with nitric acid and evaporated to dryness in a glass dish; the residue is repeatedly moistened with nitric acid and dried as thoroughly as possible. It is then extracted with a few drops of nitric acid and about 10 c.c. of distilled water, filtered, and the filtrate treated with 10 c.c. of ammonium molybdate solution, to which nitric acid has been carefully added until the precipitate formed in the first instance is just dissolved, and the whole warmed to 60°-80°. In presence of phosphoric acid a yellow, heavy precipitate is formed, either at once or after standing for some time.

Carbonic Acid

Natural waters usually contain but little free carbonic acid, the greater part being combined in the form of bicarbonates. As these latter compounds easily give up half of their carbon dioxide, a distinction is made between half and completely combined carbonic acid.

The presence of carbonic acid in water is detected by the white turbidity formed on addition of clear lime water.

To test for free carbonic acid, 1 c.c. of distilled water is treated with one drop of phenolphthalein solution and one drop of very dilute sodium hydroxide solution, and from 5 to 20 c.c. of the water under examination then added to the rose-red liquid so obtained; if decolorisation takes place in a few minutes, free carbonic acid is present. Any acidity due to peat acids should be determined in a separate portion of the sample after boiling off the carbonic acid.

To test for combined carbonic acid—that is, for bicarbonates—1 c.c. of distilled water is treated with a drop of methyl orange solution and a drop of very dilute hydrochloric acid and from 5 to 20 c.c. of the sample then added to the red solution obtained in this way; if the colour is changed to yellow, bicarbonates are present.

Trillich[1] gives the following volumetric method for the quantitative determination of free carbonic acid. A 100 c.c. measuring-flask, the mark of which is situated low down on the neck, is filled with the water to be examined by passing it through the flask for some time, so as to remove the water entering first, which loses some carbon dioxide through contact with the air (*cf.* p. 411). The water above the mark is removed by means of a pipette, ten drops of alcoholic phenolphthalein solution added, followed by *N*/10 sodium carbonate solution, which is added drop by drop until the liquid has attained a pale rose colour which, after carefully inverting the stoppered flask once, remains permanent for five minutes. Each c.c. of sodium carbonate solution used corresponds to 1·11 c.c. or 2·2 mg. CO_2.

To obtain the total volume of combined carbonic acid, that is, the sum of the half combined and completely combined carbonic acid in c.c. per litre of water, the number of c.c. of *N*/10 hydrochloric acid used in the determination of the "Alkalinity" (p. 390) is multiplied by 22·3; multiplying by 44 gives the carbon dioxide in mg. per litre of water.

The sum of the free and combined carbonic acid gives the total carbonic acid. The above methods enable the combined carbonic acid to be determined accurately, but the free carbonic acid only approximately; the value found for the total quantity of carbonic acid is

[1] *Die Münchener Hochquellenleitung aus dem Mangfalltale*, 1890, II., p. 63. *Anleitung zu hygienischen Untersuchungen*, Emmerich and Trillich, 3rd ed., p. 120.

accordingly also only approximate, but it is sufficiently correct to meet the requirements ordinarily demanded in an analysis of drinking water.

An exact determination of the total carbonic acid can be made either gas-volumetrically by the Lunge-Marchlewski method (Vol. I., p. 615), or by the following gravimetric method, in which it is expelled by hydrogen generated in a given volume of the water, and weighed after absorption.[1] The total carbon dioxide can also be determined by Adeney's method (p. 432).

The water is collected at the source of supply in the stoppered bottle *a* (Fig. 72) of 500 to 600 c.c. capacity, particular care being taken that no water which has been in contact with the atmosphere remains in the bottle. After filling the bottle to overflowing it is stoppered, and the stopper fastened down with a thin piece of sheet rubber. For the determination, the stopper is replaced by the cylinder *b* and 20 g. of granulated zinc added; it is preferable to put the zinc in the bottle before charging with the water, and allow for its volume; 20 g. zinc = 2·5 c.c. The zinc should be previously washed, first with dilute hydrochloric acid and then with water, to remove any adherent zinc carbonate. The dropping-funnel *c* is then placed in position on *b*, as shown, and a calcium chloride tube attached at *d*; the other end of the calcium chloride tube is connected with a weighed potassium hydroxide absorption apparatus. Fifty c.c. of 20 per cent. hydrochloric acid, to which a drop of platinum chloride solution has been added, is then gradually run into *a* through the dropping-funnel *c*, about an hour being taken for the addition. After the hydrogen has been generated for three hours the carbon dioxide is completely expelled. Finally, the hydrogen in the absorption apparatus is removed by passing a current of dry air, free from carbon dioxide. The increase in weight of the absorption apparatus gives the weight of total carbon dioxide present in the water; 1 g. CO_2 = 506·4 c.c.

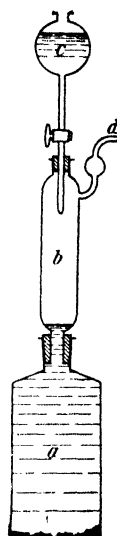



Fig. 72.

Calcium and Magnesium

These substances are determined gravimetrically by the usual methods (*cf.* p. 457 *et seq.*).

The calcium can also be estimated volumetrically by Mohr's method, in which it is precipitated as calcium oxalate with an excess of titrated oxalic acid solution, and the excess of oxalic acid titrated back with potassium permanganate solution. The method is sufficiently exact for most hygienic purposes.

[1] L. W. Winkler, *Z. anal. Chem.*, 1903, 42, 735.

The magnesium can also be determined volumetrically. Of the various methods which have been proposed, that of Pfeifer[1] is carried out as follows:—

One hundred c.c. of the water is titrated, whilst boiling, with *N*/10 acid with addition of alizarin, as in Wartha's method for the determination of alkalinity (p. 391). The water, which is then free from carbon dioxide, is rinsed with boiled distilled water into a 200 c.c. graduated flask and treated with a measured excess (25 to 50 c.c.) of lime water; the flask is filled to 5 c.c. above the mark, closed with a rubber stopper, well shaken, cooled after a few minutes, and then the liquid poured on to a large pleated filter. The excess of calcium hydroxide is titrated back in 100 c.c. of the filtrate. The content of magnesium is calculated from the amount of calcium hydroxide used up; 1 c.c. of *N*/10 calcium hydroxide solution corresponds to 2·0 mg. MgO.

This method, if carried out with a little care, gives quite satisfactory results. It is important to use sufficient excess of the precipitant. The strength of the lime water should be checked by a blank experiment, in order to eliminate experimental errors.

The total hardness of the water can be calculated (*cf.* p. 391) from the quantities of calcium and magnesium determined gravimetrically or volumetrically.

Sodium and Potassium

An ordinary water contains only minute quantities of sodium and potassium, the quantity of the former being almost always many times greater than that of the latter. These constituents of natural waters are generally of but little importance, either from a hygienic or technical standpoint; accordingly their direct estimation[2] is seldom undertaken.

If the calcium, magnesium, the total combined carbonic acid, sulphuric acid, nitric acid and chlorine have been determined, the amount of the alkalis can be calculated. The result is certainly not exact, as with most determinations by difference, but it is sufficiently correct for most purposes.

To arrive thus at the quantity of alkalis present, the quantities of bases and of acids found are divided by their equivalents and the quotients obtained for the bases and acids respectively added together. If the water contains alkalis, the sum of the quotients from the bases will be smaller than the sum of those from the acids, and the difference multiplied by the equivalent weight of sodium oxide will give the amount of alkali in terms of Na_2O.

[1] *Z. angew. Chem.*, 1902, 15, 199.

[2] *Cf.* Thresh and Beale, *loc. cit.*, p. 340; also, Tiemann-Gärtner, *loc. cit.*, p. 108.

The following data of the water supplied to Budapest (April 1901) will serve as an example of the calculation. The subjoined table gives the analytical results, the equivalent weights of the bases and acids and their quotients :—

	In 1000 c.c. Water.	Equivalent Weights.	Quotients.	
Calcium oxide	77·8 mg.	$\frac{1}{2}$ CaO = 28·0	2·78	4·00
Magnesium oxide	24·3 "	$\frac{1}{2}$ MgO = 20·0	1·22	
Chlorine *	3·7 "	Cl = 35·5	0·10	4·37
Sulphur trioxide	28·9 "	$\frac{1}{2}$ SO_3 = 40·0	0·72	
Nitric anhydride	4·5 "	$\frac{1}{2}$ N_2O_5 = 54·0	0·08	
Combined carbon dioxide	76·3 "	$\frac{1}{2}$ CO_2 = 22·0	3·47	

* *It would be more correct, as dualistic formulæ are used, to express this as hydrochloric acid, and not as chlorine. But as the amount of chlorine is never expressed as hydrochloric acid in the results of water analyses, it is preferable to leave it as chlorine, especially as this has no influence on the value of the quotient.*

The totals 4·00 and 4·37 differ by 0·37 ; this number multiplied by the equivalent weight of sodium oxide = 31, gives 11·5 mg. Na_2O per litre.

Ammonia and nitrous acid, etc., need only be taken into consideration if present in comparatively large quantity. Silica, though present in all waters, is of no consequence, as the silicic acid has no effect on methyl orange in the determination of the alkalinity.[1]

Ammoniacal Nitrogen

The solution first recommended by J. Nessler, which consists of the double compound of potassium and mercuric iodides (K_2HgI_4) in potassium or sodium hydroxide solution, forms an extremely sensitive reagent for the detection of ammonia. It gives a strong brownish-yellow coloration with extremely dilute ammonia solutions ; the reaction is so sensitive that 0·05 mg. of ammonia in 1 litre of water can be detected. As, however, most natural waters contain considerable quantities of calcium and magnesium salts, a precipitate of calcium carbonate and magnesium hydroxide is formed on addition of this reagent, which exercises a very disturbing effect in testing for very small quantities of ammonia. In order, therefore, to test for ammonia in natural waters it is necessary either first to remove the calcium and magnesium compounds by means of sodium hydroxide solution or to prevent their precipitation by the use of Rochelle salt; the latter procedure is certainly the simpler.

Nessler's Reagent as used for the detection and colorimetric estimation of ammonia is made up as follows :[2]—

62·5 g. of potassium iodide is dissolved in about 250 c.c. of distilled water, 10 c.c. of this solution is set aside, and into the remainder is

[1] See Thresh and Beale, *loc. cit.*, p. 349.
[2] *Cf.* Fowler, *Sewage Works Analyses*, p. 41.

carefully run a cold saturated solution of mercuric chloride. A brilliant red precipitate of mercuric iodide is formed, which at first quickly redissolves on shaking. The addition is continued till a permanent precipitate is obtained. This is redissolved by the potassium iodide held in reserve, and more mercuric chloride is added, drop by drop, until, after stirring, a red opalescence remains. One hundred and fifty g. of potassium hydroxide, dissolved in distilled water and allowed to cool, is then added gradually, with continued shaking, to the opalescent solution. The whole is made up to 1 litre, allowed to settle and the clear liquid decanted into a bottle.

The Nessler solution improves on keeping, and should therefore be made up some time before it is required for use. Special attention must be given to the endpoint of the addition of the mercuric chloride to the iodide solution. If the potassium iodide is in excess, the reagent will not be delicate, and the coloration with ammonia will be a long time in reaching its full intensity. On the other hand, the addition of an excess of mercuric chloride will give an excess of mercuric iodide, which will dissolve when the potassium hydroxide is added, and the reagent will be exceedingly delicate and the full coloration will be obtained rapidly. The solution is liable, after the ammonia tubes have stood for about ten minutes, or even less, to become turbid and deposit a red crystalline precipitate, so that, whilst maximum delicacy is required, this turbidity is to be avoided. Practice is the only guide to making up a good Nessler solution: 1 c.c. of the solution should give a coloration with 0·008 mg. NH_3 = 0·8 c.c. $N/100$ ammonium chloride solution in 50 c.c. of pure water.

Rochelle Salt Solution. Fifty g. of crystallised Rochelle salt is dissolved in 100 c.c. of warm water, and 5 c.c. of Nessler's reagent added to the filtered solution in order to prevent the formation of mould. Also, the solution should be kept in the dark. As commercial Rochelle salt almost always contains traces of ammonia, the liquid is yellowish at first, but becomes colourless on standing for from two to three days.

If it is necessary to filter the above Rochelle salt solution or the Nessler reagent itself, this is best done through a small plug of cotton-wool, rejecting the first portions of the filtrate.

For the detection of ammonia, 50 c.c. of the water to be examined is treated with 1 c.c. of the Rochelle salt solution and 1 c.c. of Nessler's reagent in a cylinder of colourless glass, and the colour of the liquid then observed by looking down through it obliquely on to a sheet of white paper placed below. If the water was originally colourless, a yellow or brownish-yellow tint is produced in presence of the smallest traces of ammonia.

The quantitative colorimetric estimation [1] is carried out as follows:—

[1] *Cf.* L. W. Winkler, *Chem. Zeit.*, 1899, 23, 454 and 541; 1901, 25, 586.

Two glass-stoppered bottles each of about 150 c.c. capacity are required; cut-glass bottles are the most suitable, as they permit of the clearest observation of the colour. Glass cylinders about 4 cm. wide and 20 cm. high may also be used. One hundred c.c. of the water to be examined is placed in one of the bottles and the same quantity of ordinary water free from ammonia, or of distilled water, in the second; to each is then added 2 to 3 c.c. of Rochelle salt solution, followed, drop by drop, by the same quantity of Nessler's reagent, with stirring. A standard ammonium chloride solution, of which each c.c. is equivalent to 0·1 mg. NH_3, is then added drop by drop from a narrow burette, with shaking, to the contents of the bottle containing the ammonia-free water, until the colour of the two liquids is identical. The number of c.c. of ammonium chloride solution used gives the content of ammonia in the water under examination, in mg. per litre.

The ammonium chloride solution used for the estimation is prepared by dissolving 0·315 g. pure dry ammonium chloride in water and making up to 1 litre.

More exact results may be obtained by preparing a set of standard tubes either from Nessler's reagent with varying quantities of standard ammonium chloride solution, or from permanent standards made by mixing solutions of platinum and cobalt salts.[1]

The ammonia is then determined by adding 2 c.c. of Nessler's reagent to 50 c.c. of the sample and comparing the coloration with an equal volume of the standard mixture. It is important that the temperature of the sample and of the standard should be as nearly as possible the same.

The reagents (Nessler solution and Rochelle salt) cannot be kept ready mixed, because even after standing for one day crystalline mercurous iodide begins to separate in golden yellow scales, the quantity of which steadily increases; the reagent is then no longer suitable for the colorimetric estimation of ammonia, as it gives a turbidity as well as a coloration. The best plan is to mix equal volumes of the two reagents as required, and to use 5 c.c. of the mixture for each experiment; this mixture is referred to as the "mixed reagent." The 5 c.c. of mixed reagent should be added to the 100 c.c. of water drop by drop, not all at once, as in the latter case a lemon yellow coloration is often obtained instead of a brownish-yellow, which is prejudicial to the colorimetric comparison. Should the use of the mixed reagent cause a precipitation of mercuric iodide, which is usually due to the use of freshly prepared Nessler's reagent, 0·1 to 0·2 g. of potassium iodide are dissolved in 50 c.c. of the latter; a larger addition of potassium iodide diminishes the sensitiveness of the test.

[1] *Cf.* Report of American Committee on Water Analysis, *loc. cit.*, p. 16.

Natural water is more suitable for comparison than distilled water, as the latter is usually less easily obtained free from ammonia. According to Winkler, the distilled water of laboratories often contains ammonia, which is only exceptionally derived directly from the air, being more probably due to the action of bacteria.

If the water under examination is turbid it must be filtered; it is advisable to use a small filter paper and to reject the first 100 to 200 c.c. of the filtrate, which may have absorbed ammonia from the paper. If the water is very hard the mixed reagent causes a precipitate of the tartrates of the alkaline earths; 100 c.c. of the water must then first be mixed with 5 c.c. of the Rochelle salt solution and after that with the mixed reagent.

The colorimetric determination cannot, of course, be made without preliminary treatment if the sample is coloured. It is sometimes possible to obtain a colourless liquid by adding to 500 c.c. of the water 1 c.c. of sodium hydroxide solution and an equal quantity of sodium carbonate solution, as the precipitate which is thus formed may carry down the coloured ingredients. If this method of decolorisation fails, that proposed by Miller[1] should be used, according to which the ammonia is distilled off, after addition of sodium carbonate, either with or without previous dilution, and determined colorimetrically in the distillate with Nessler's reagent. Special care must be taken in this case to be sure that the apparatus used is perfectly clean. The water under examination must fill at least two-thirds of the retort used for the distillation, and not more than two-fifths of the original volume of the water is distilled over. Emmerling[2] recommends that, in presence of albumen, the water should always be distilled for the determination of ammonia, as the direct determination in such samples is always inexact.

Should larger quantities of ammonia be present, which very rarely occurs in an ordinary water supply, the sample may be distilled with sodium carbonate and the liberated ammonia determined in the distillate either alkalimetrically or by precipitation as ammonium platinichloride, with subsequent ignition and weighing of the residual platinum.[3]

Albuminoid and Proteid Nitrogen

The nitrogenous organic substances which contaminate natural waters are of varying origin. Urea, hippuric acid, and uric acid may be introduced from human urine, or from that of carnivorous or vegetarian animals; leucine, tyrosine, aspartic acid, glutaminic acid, indole, skatole, etc., from excrements or from decay of albumins of either vegetable or of animal origin. Some idea of the amount of

[1] *J. Chem. Soc.*, 1849-50, 3, 117. [2] *Ber.*, 1902, 35, 2291.
[3] *Cf.* Tiemann-Gärtner, *loc. cit.*, p. 125.

nitrogenous organic matter is obtained by the determination of the so-called *Albuminoid Ammonia*[1] as originally termed, but as already explained best referred to as *Albuminoid Nitrogen*. This is done by distilling a measured sample of the water with a strongly alkaline potassium manganate solution and estimating the amount of ammonia in the distillate. The amount of nitrogenous organic impurities, in solution and suspension in water, may also be determined by oxidising with potassium persulphate in acid solution, and then determining the amount of ammonia formed colorimetrically in the liquid, thus avoiding a distillation. This is known as the determination of the *Proteid Nitrogen*.[2] It is important to recognise that these determinations do not permit of the calculation of the absolute amount of nitrogenous organic matter present; the results obtained serve only as a guide to the proportions of these substances.

Albuminoid Nitrogen.—The determination of albuminoid nitrogen is conveniently combined with the estimation of the inorganic nitrogen ("free ammonia" or ammoniacal nitrogen) present as such in the water. Miller's distillation method is employed for the determination (p. 416). In addition to the reagents already described for the determination of ammoniacal nitrogen, an alkaline potassium manganate solution is required; this is best made up in quantities of 3 litres as follows:—Twenty-four g. of potassium permanganate is dissolved in about 500 c.c. of tap water, 600 g. of potassium hydroxide is separately dissolved (preferably in an earthenware or clean iron dish) and the solutions mixed and thoroughly boiled in a flask. This is best done in quantities not exceeding a litre (in case of breakage). The boiled solutions are then mixed and made up to 3 litres with distilled water free from ammonia.

The determination is carried out in a tubulated retort of rather more than 1 litre capacity, the tubulure of which is provided with a ground glass stopper. It is so connected with a condenser that the neck of the retort points somewhat obliquely upwards, and the condenser obliquely downwards; the neck of the retort is bent downwards at an obtuse angle at the end, and is drawn out so that it has the same diameter as the inner tube of the condenser, with which it is connected by a piece of boiled-out, black rubber tubing, in such a way that glass touches glass, and the steam comes into contact with the rubber as little as possible. Five hundred c.c. of the water under investigation is poured into the retort through the tubulure. Should the sample be acid, a little freshly ignited sodium carbonate must be added, in order to liberate the free ammonia, but this addition is

[1] Cf. *Water Analysis*, by J. A. Wanklyn and E. T. Chapman, *loc. cit.*, p. 28; also, Tiemann-Gärtner, *loc. cit.*, p. 263.

[2] L. W. Winkler, *Z. anal. Chem.*, 1902, 42, 290.

usually unnecessary, as an ordinary water supply generally contains alkaline earth carbonates. The liquid is then distilled as quickly as possible, by heating the retort, carefully, with the naked flame of a large burner, or over strongly heated wire gauze. The distillate is collected in two fractions, each of 100 c.c. in large Nessler glasses, and the distillation momentarily stopped when the second glass is full. The two glasses contain the whole of the free ammonia in the 500 c.c. of water, which is determined colorimetrically with Nessler's reagent.

After allowing to cool for a short time, the stopper of the retort is removed, and 50 c.c. of the strongly alkaline potassium manganate solution poured into the liquid, with gentle shaking, through a carefully cleaned glass funnel. The retort is then closed and the distillation resumed, two further fractions of 100 c.c. each being collected. This distillate contains the ammonia formed from the nitrogenous organic compounds, and is also colorimetrically estimated with Nessler's reagent.

Proteid Nitrogen.—The following solutions are required for the determination of proteid nitrogen in natural water:[1]—

1. *Potassium Persulphate Solution.* Commercial potassium persulphate usually contains considerable quantities of the ammonium salt, and must therefore be purified. For this purpose 15 g. of the salt is powdered and dissolved in 100 c.c. of water at 50° to 60°, with addition of 1·5 g. of potassium hydroxide. The solution is filtered through a small plug of cotton-wool, and allowed to stand in a cool place for a few hours. The crystals which separate are collected, washed with cold water and dried at the ordinary temperature. For use, 1 g. of the pure, powdered persulphate is dissolved in 100 c.c. of water. The solution does not keep long, so that large quantities should not be made up. The fresh solution is neutral, and gives no turbidity with barium chloride; a decomposed solution contains potassium hydrogen sulphate, gives an acid reaction, and is precipitated by barium chloride.

2. *Approximately N/5 Sulphuric Acid.* Six c.c. of pure concentrated sulphuric acid is diluted with water to 1 litre.

The reagents used for the determination of the liberated ammonia are the same as those required for the estimation of free ammonia.

The determination of proteid nitrogen is carried out as follows:—A flask of about 200 c.c. capacity is first rinsed out with the water to be examined, and 100 c.c. of the sample then introduced; 5 c.c. of *N*/5 sulphuric acid, and 5 c.c. of the potassium persulphate solution are then added. The liquid should then be acid; if it is not, 5 c.c. more of the sulphuric acid is added. The flask is placed in a water-bath, in which the water is boiling vigorously, so that the whole of the lower portion of the flask is exposed to the steam, and the neck covered

[1] *Cf.* L. W. Winkler, *Z. anal. Chem.*, 1902, 42, 295.

with a small beaker to prevent any appreciable loss by evaporation. After remaining on the water-bath for fifteen minutes, the flask is removed and the contents cooled completely by running water. The liquid is then poured into a cut-glass bottle of about 150 c.c. capacity, or into a Nessler cylinder, and 5 c.c. of the "mixed" Nessler reagent (p. 415) added drop by drop. A separate 100 c.c. of the sample is also poured into a similar bottle or cylinder, and treated with 5 or 10 c.c. of *N*/5 sulphuric acid, 5 c.c. of the mixed Nessler reagent added drop by drop, and 5 c.c. of the potassium persulphate solution. The latter liquid will be slightly coloured, whilst the sample which has been heated will be darker according to the proportion of ammonia present. To determine the amount of proteid nitrogen, ammonium chloride solution (1 c.c. = 0·1 mg. NH_3) is added drop by drop to the less strongly coloured solution until the colorations are equal. The number of c.c. of ammonium chloride solution required to effect this gives the amount of proteid nitrogen in mg. per litre of the original water.

The addition of sulphuric acid and persulphate solution to the solution used for comparison is important, as the reagents almost always contains traces of ammonia which would cause considerable error. This is avoided by the above method of procedure; also the proteid nitrogen is determined independently of any free ammonia in the original water, as this is present in equal amount in both of the liquids under comparison.

The proteid nitrogen determination is especially applicable to the analysis of drinking water.

The determination of albuminoid nitrogen is more suitable for turbid and coloured waters. The proteid nitrogen determination can be carried out with waters which have been filtered, and if necessary diluted, but the values found refer only to the dissolved nitrogenous matter, and not to that present in suspension.

The most minute amounts of substances of animal origin present in water can be detected with certainty by means of a proteid ammonia estimation; if, for instance, 10 c.c. of urine is added to 1 cubic metre of water, 0·1 mg. of proteid nitrogen per litre will be found, even after a lapse of several weeks.

Experiment has shown, however, that on the gradual oxidation of a polluted water the rate of reduction of the albuminoid and proteid nitrogen was practically the same.

Iron

Iron is usually present in water, in solution as ferrous hydrogen carbonate; on standing in the air it is precipitated as insoluble brownish-red ferric hydroxide. In testing water for iron it is therefore necessary to note whether the iron has already separated in the form of

flocculent particles; if so, the yellowish-brown sediment must be collected on a filter, digested with hot, dilute hydrochloric acid, free from iron, and the solution tested for iron, after dilution, with potassium ferrocyanide or with ammonium thiocyanate.

If the iron is in solution, it is best tested for qualitatively by adding a few drops of sulphuretted hydrogen water and 1 to 2 drops of ammonia to 100 c.c. of the sample; 0·1 mg. of ferrous iron in the 100 c.c. gives a distinct brown, and 0·01 mg. a perceptible coloration. To make sure that the reaction is not due to traces of lead or copper, acetic acid is added to the brown liquid till acid; the coloration is destroyed if due only to iron, otherwise lead or copper is present. The reaction of ammonium sulphide with ferric iron is far less sensitive. A very dilute solution of a ferrous or ferric salt is coloured bluish-green by ammonium sulphide, in presence of much ammonia.

Iron is determined quantitatively either by titration or colorimetrically according as to whether it is present in appreciable quantity or only in traces; the latter method is usually preferable.

For the volumetric estimation from 500 to 1000 c.c. of the water is evaporated to dryness in a glass dish with a few c.c. of hydrochloric acid and 0·1 to 0·2 g. of potassium chlorate, which is added to destroy organic matter. If the iron has separated out through long standing, the entire contents of the sample bottle are used for the determination and the volume of the water found by subsequently calibrating the bottle. The bottle must be rinsed repeatedly with warm hydrochloric acid so as to remove completely any iron compounds adhering to the sides. The residue from the evaporation is warmed for some time on the water-bath with 20 c.c. of dilute sulphuric acid, the solution filtered from undissolved gypsum, silica, etc., and the residue washed with 10 to 20 c.c. of hot water. The iron in the filtrate and washings is then reduced with zinc or magnesium free from iron and titrated with *N*/100 potassium permanganate solution (*cf.* p. 175).

To determine iron colorimetrically, either with potassium ferrocyanide or with ammonium thiocyanate, the ferrous iron must of course be first oxidised to the ferric condition; this is effected by means of hydrochloric acid and potassium chlorate as described above. The residue obtained on evaporation is dissolved in a few drops of hydrochloric acid, diluted with distilled water to 100 c.c., and the coloration produced on addition of potassium ferrocyanide or of ammonium thiocyanate compared with that obtained by adding progressively increasing quantities of ferric iron and the same volume of the reagent to 100 c.c. of distilled water[1] (*cf.* p. 171).

A very delicate method for determining small quantities of iron is described by O. Mayer:[2]—To 100 c.c. of the water is added at

[1] *Cf.* Tiemann-Gärtner, *loc. cit.*, p. 80. [2] *Monit. Scient.*, 1913, 3, 81-82.

least 10 to 20 drops of a solution of 1 c.c. of bromine in 500 c.c. of concentrated hydrochloric acid, 20 to 40 drops of a solution of 250 g. of ammonium or potassium thiocyanate in 500 c.c. of distilled water, and 10 c.c. of a mixture of equal volumes of ether and amyl alcohol. The mixture is gently agitated in a stoppered cylinder, after which on allowing it to stand, the amyl alcohol rapidly rises to the surface, carrying any iron with it in the form of thiocyanate, which is soluble in amyl alcohol. A content of 0·001 mg. of iron per litre can be detected by this method. In order to estimate the iron a comparison is made with the colour produced by adding a standard solution of iron[1] (40 c.c. of the solution diluted with distilled water to 100 c.c.) drop by drop to a mixture of 95 c.c. of distilled water, 10 c.c. of acid indicator and 10 c.c. of ether-amyl alcohol mixture. This method gives total iron; to estimate ferric iron evaporation is carried out with hydrochloric acid only (instead of in presence of bromine); ferrous iron is found by difference.

Whenever possible, the iron should be estimated at the source of supply in a freshly collected sample of the water. The method can then be simplified by omitting the oxidation and determining the ferrous iron colorimetrically with ammonium sulphide.[2] The following method is specially suitable for a continuous series of observations such as is required in testing a process for the removal of iron.

The solution employed as a standard for comparison is prepared by dissolving 0·7 g. of ferrous ammonium sulphate and 1 c.c. of dilute sulphuric acid in 1 litre of sulphuretted hydrogen water; 1 c.c. of this solution contains 0·1 mg. Fe. The solution must be kept in well-closed vessels, and should not be used after it ceases to smell of sulphuretted hydrogen; it is best to divide it up in small bottles, closed with sound corks and sealed with paraffin-wax. In this way the solution can be kept unchanged for years; a solution which has spoilt by standing can be regenerated by saturation with sulphuretted hydrogen.

For the determination, 100 c.c. of the water is treated with 5 c.c. of sulphuretted hydrogen solution, and 1 to 2 drops of ammonia in a colourless glass cylinder, about 4 cm. wide and 20 cm. high. One hundred c.c. of distilled water is similarly treated also with 5 c.c. of sulphuretted hydrogen solution and 1 to 2 drops of ammonia, and the standard ferrous ammonium sulphate solution then added drop by drop, with shaking, until the depth of colour of the two liquids is approximately equal; the comparison cannot be taken as correct at this stage, as the sample is coloured brown whilst the standard

[1] 0·2251 of ferric potassium sulphate or 0·2157 g. of ferric ammonium sulphate in a litre of distilled water, containing 10 c.c. of hydrochloric or sulphuric acid.

[2] L. W. Winkler, *Z. anal. Chem.*, 1902, 41, 550.

inclines to a bluish-black. To the latter, 2 to 3 drops of dilute hydrochloric acid are therefore added, followed, after decolorisation, by a few drops of aqueous ammonia, which bring back the coloration to the brown tint of the sample; a further quantity of the ferrous ammonium sulphate solution is then added until the colorations are equal. Finally, both liquids are decolorised by adding a few drops of dilute hydrochloric acid and the colour regenerated with ammonia, when the two colorations should again be equal. The amount of iron present in mg. per litre of the original sample is equal to the number of c.c. of the ferrous ammonium sulphate solution used.

This method gives accurate results only if the water under examination contains from 0·3 to 1·5 mg. of ferrous iron per litre; if the quantity of iron is less than 0·3 mg. per litre the colorimetric comparison is made in higher and rather wider cylinders with 500 c.c. of the water, and if greater than 1·5 mg. per litre, a measured volume of the water, to which a few c.c. of sulphuretted hydrogen water have been added, and which is therefore deeply coloured, is correspondingly diluted for the comparison.

To carry out this determination in the laboratory the iron is kept in the ferrous condition by acidifying the water in the collecting vessel with a few drops of hydrochloric acid and adding 10 c.c. of 10 per cent. sulphuretted hydrogen water; no oxidation to ferric iron occurs as long as the water smells of sulphuretted hydrogen. The colorimetric comparison is then carried out with 110 c.c. instead of with 100 c.c. of water. If the sample also contains lead it is treated as above with hydrochloric acid and sulphuretted hydrogen solution, allowed to stand over night, the water then decanted from the precipitated lead sulphide and sulphur, and estimated as above.

Should it be necessary to determine how much iron is present in solution and in suspension respectively, the water is treated with 50 c.c. of sulphuretted hydrogen solution per litre, without addition of acid, and filtered; the ferrous sulphide formed is at first in the colloidal condition and is not retained in perceptible amount by the filter paper. One hundred and five c.c. of the filtrate is then taken for the colorimetric estimation, which thus gives the dissolved iron; this deducted from the total iron gives the insoluble iron by difference.

The total iron may be determined by the above method, but the ferric iron must first be reduced with sulphuretted hydrogen to ferrous iron. From 10 to 500 c.c. of the water, according to the amount of iron present, is evaporated to dryness in a glass dish with a few c.c. of hydrochloric acid and 0·1 g. of potassium chlorate. The residue is warmed on the water-bath for a few minutes with a few drops of hydrochloric acid and about 10 c.c. of water, and about 5 c.c. of sulphuretted hydrogen water added to the liquid while it is still warm.

After cooling it is filtered through a small filter, and washed with distilled water until the volume of the filtrate is 100 c.c. The iron is then determined in the filtrate as described above. The filtrate is somewhat opalescent, owing to the presence of finely divided sulphur, but this is of no consequence, as on addition of the sulphuretted hydrogen water and ammonia the sulphur dissolves in the ammonium sulphide which is formed.

If the water is coloured this process need not be modified, as the coloured substances are destroyed by the chlorine which is generated.

Manganese

The following method described by Lübrig[1] for the detection of manganese has been found satisfactory:—

One hundred c.c. of water is mixed with 3 c.c. of concentrated nitric acid and sufficient silver nitrate to precipitate the chlorides, then 3 g. of ammonium persulphate in strong solution is added, and the liquid heated to boiling for five minutes. If manganese compounds are present, the colour of permanganate is produced, and as little as 0·005 mg. can be detected. By comparing the colour with that given by a standard solution, the method can be made quantitative. The distilled water used must be purified by oxidation and redistillation. As a standard, permanganate solution, freshly prepared with the special distilled water and containing about 0·05 to 0·10 mg. per c.c., may be used.

In the absence of nitrites the liberation of iodine from potassium iodide is sufficient, according to Thresh,[2] to detect 1 part of manganese as manganic salt in 10 million parts of water.

Copper, Zinc, Tin, Aluminium

It is seldom that either of the first three metals occur in drinking water. Traces of copper may be present from the use of copper salts as algicides in reservoirs. Any appreciable quantity can be detected, at any rate after concentration by evaporation, by means of the blue colour given on addition of ammonia.

Zinc and tin may occasionally be present from water pipes coated with zinc or tin and may be detected by precipitation as sulphides after concentration.

A good method for the detection and estimation of small quantities of aluminium is desirable in view of the very general use of aluminium salts in the clarification of water. A method described by F. W. Atack[3] has possibilities. The reagent used is the sodium salt of alizarine mono-sulphonic acid, in 0·1 per cent. aqueous solution. The

[1] *Chem. Zeit.*, 1914, 38, 781. [2] *Loc. cit.*, p. 315. [3] *Analyst*, 1915, 50, 512.

solution is filtered before use, and is pale yellow in presence of acids and purple on making alkaline.

To detect aluminium, 5 c.c. of the solution is taken and 1 c.c. of the reagent added and then ammonia until the solution is alkaline, as shown by the purple colour. The solution is boiled, cooled and acidified with acetic acid, a red precipitate or coloration is conclusive evidence of the presence of aluminium.

Calcium and magnesium salts do not affect the test as their salts are soluble in presence of acetic acid. Iron is prevented from interfering by the addition of a citrate to the original solution, acidified with hydrochloric acid. The test is stated to detect the presence of 1 part of aluminium in 10 million parts of water.

To estimate the aluminium, from 5 to 20 c.c. of the solution (containing 0·005 to 0·05 mg. of aluminium) is acidified with hydrochloric acid, 10 c.c. of glycerol and 5 c.c. of the reagent added, the solution diluted with distilled water to 40 c.c. and then rendered slightly ammoniacal. After standing for five minutes, the solution is acidified with acetic acid, the latter being added until no further change in the coloration occurs. The mixture is then diluted to 50 c.c. and compared with a standard.

It has been found that lac-dye (laccainic acid) behaves similarly to the alizarine salt above described, and useful comparative results have been obtained in water-works practice in determining the amount of aluminium in the water after coagulation and filtration. In this case, concentration by evaporation may be avoided by employing tall litre capacity cylinders in which to make the comparative colorimetric tests. In order to obtain tints of the same character, the standard solution for comparison must, in this case, be made up with the raw water (filtered from visible suspended matter) rather than with distilled water.

Lead

Lead may be introduced into a water supply through the material of the mains and pipes; although the quantities thus dissolved are small, they are by no means indifferent from a hygienic standpoint. The lead is present in the water as dissolved lead hydrogen carbonate; on standing in the air, or on boiling, the lead is precipitated together with the calcium carbonate.

To test qualitatively for lead, 100 c.c. of the water is poured into a beaker, acidified with acetic acid, and treated with a few c.c. of sulphuretted hydrogen water; the liquid is coloured brownish-yellow even if the water only contains a few tenths of a mg. of lead per litre. The presence of iron does not interfere, as it does not react with hydrogen sulphide in acid solution.

If the water contains only 0·1 mg. or less lead per litre, it must be concentrated by evaporation. G. Frerichs[1] has made the very important observation, that if water containing lead is filtered through pure cotton-wool the lead is completely retained and the water thus freed from lead. This property of cotton-wool can be utilised for the qualitative detection and for the quantitative estimation of even the smallest quantities of lead in water. For the detection of very small quantities of lead the following method may be adopted:—

A plug of cotton-wool weighing 0·5 to 1 g. is pressed into a glass funnel and moistened with distilled water so that it adheres to the funnel. About 1 litre of the water is then filtered through the cotton-wool. To redissolve the retained lead a mixture of 10 c.c. of distilled water and 1 c.c. of dilute acetic acid is heated to boiling and poured, one c.c. at a time, on to the cotton-wool; the acid liquid completely removes the lead, so that the filtrate gives a strong reaction with sulphuretted hydrogen water even if only traces of lead are present, as the lead is concentrated nearly a hundredfold by this method. In order to be certain that the reaction is not due to copper the process is repeated, but instead of adding sulphuretted hydrogen water to the acetic acid filtrate, an excess of ammonia is added. The solution is then warmed, filtered to remove any iron which may be present, and evaporated to dryness in a very small glass dish; the residue is dissolved in a drop of hydrochloric acid and a few drops of water, and tested for copper with potassium ferrocyanide.

The quantitative estimation of lead is also based on the reaction with sulphuretted hydrogen, and is carried out colorimetrically. A lead solution containing 0·1 mg. lead per c.c. serves as a standard, and is prepared by dissolving 0·16 g. of dry powdered lead nitrate in distilled water and making up to 1 litre. Quantities of 0·5, 1·0, and 1·5 c.c., or of 1·5, 2·0, and 2·5 c.c. of this lead solution, according to the depth of colour observed in the qualitative test, are each diluted in colourless beakers with water free from lead up to 100 c.c., and acidified with 1 c.c. of acetic acid. One hundred c.c. of the sample is poured into a similar beaker, also acidified with 1 c.c. of acetic acid, and 10 c.c. of sulphuretted hydrogen water then added to the contents of each beaker, and the colorations compared. If only traces of lead are present it is concentrated by Frerichs' method as described above. To secure accuracy 1 litre of the water is filtered several times successively through the cotton-wool. After dissolving the lead in hot water containing acetic acid, washing is continued with water free from lead until the volume of the liquid amounts to 100 c.c. The colorimetric determination is then carried out with this tenfold concentrated solution.

If the water is coloured it must be decolorised previous to the

[1] *Apoth. Zeit.*, 1902, 884.

determination of lead. One hundred c.c. is acidified with a few drops of hydrochloric acid, a few c.c. of chlorine water added and the liquid boiled in a conical flask until the excess of chlorine is expelled; ammonia is then added to the cold solution until it is just alkaline, the whole diluted to 100 c.c., 1 c.c. of dilute acetic acid added, and the colorimetric determination carried out as above.

Investigation of the Action of Various Waters on Metallic Lead

It is frequently necessary to determine the action of a given water upon lead. An extended research on this subject has been made by H. Heap at the suggestion of Prof. Delépine.[1] In Heaps' paper[2] a complete history of the subject is given.

To determine the action of various waters upon lead, Heap used both coiled lead pipes and strips of lead foil. The second method which is most convenient is described as follows:—

Special glass vessels were procured, cylindrical in shape and fitted with a broad conical stopper, so that by filling the vessel with water and inserting the stopper, water was displaced until the stopper fitted tightly, rendering the contents practically air-tight. First the bottles were well washed and steeped in acid; then washed with distilled water and left to soak in distilled water until no alkali was given up by the glass. The bottles were used only after it had been found that water kept in them for twenty-four and forty-eight hours was not alkaline and did not contain lead. The volume of liquid held by the bottles was 120 c.c. The lead used in these experiments was pure lead foil. On analysis it was found to be 99·81 per cent. of metallic lead.

The lead was polished brightly by vigorous rubbing with well washed wash-leather. The lead was cut up into pieces $6{\cdot}35 \times 2{\cdot}54 \times 0{\cdot}012$ cm. The area was practically 32·26 sq. cm.

In making an experiment the bottles were washed with the water under examination, then filled with it and a strip of lead foil inserted. The stopper was pressed in and secured and the whole apparatus placed in an incubator kept at 20° for a definite period of time, after which the apparatus was removed and the appearance of the water and lead strip noted. The stopper was now removed, the lead taken out, and the water examined for lead. In some experiments the water was kept under anaërobic conditions. The gases were pumped off by making use of Adeney's gas analysis apparatus. This apparatus offered another advantage in that various gases could easily be introduced at definite pressures to the gas-free water. In certain cases extracts and infusions of organic matter and peat were made, some

[1] Delépine, *Journal of the Royal Sanitary Institute*, 1914, **35**, No. 3, p. 117.

[2] *J. Soc. Chem. Ind.*, 1913, **32**, 771, 811, 847.

by simple digestion of the matter with water, others by percolating the water through the matter.

The method used for estimating the amount of lead in the water was as follows:—The water which had been kept in contact with the lead was poured into a Nessler glass up to the 50 c.c. mark: 0·5 c.c. of a 0·5 per cent. solution of acetic acid was added, and then 5 c.c. of a saturated aqueous solution of sulphuretted hydrogen. According to the amount of coloration produced, it was judged whether the water contained more or less than the amount of lead which can be estimated by this reaction. When the amount was too small the water was concentrated and where the lead was in too great quantity the water was diluted. The amount of coloration produced, depending upon the amount of lead present, was estimated by matching the colour with a standard solution of lead acetate and hydrogen sulphide water. The lead solution was made so that 1 c.c. contained the equivalent of 0·0001 g. of lead. A blank test was made to compensate for the natural colour of the water and variation of tints which are not due to the presence of lead. When it was wished to differentiate between lead in solution and lead in suspension, the method adopted was to estimate the total lead and afterwards filter the liquid through asbestos wool and estimate the lead in the filtrate. The difference gives the lead in suspension. Asbestos was used because ordinary cellulose filter papers absorb dissolved lead out of certain solutions. In other experiments the amount of lead disappearing from the strip was estimated by direct weighing. The reaction of the water was determined when required by titrating 100 c.c. with $N/100$ caustic soda or sulphuric acid solution, using phenolphthalein, lacmoid and methyl orange as indicators.

Where appreciable quantities of metallic impurities are present as in cases of specific pollution by metal works effluents, it is best to follow the ordinary methods of mineral analysis after suitable concentration of the sample.

The Determination of Dissolved Gases

Almost every natural water contains free carbon dioxide and air in solution. Ground water sometimes also contains small amounts of hydrogen sulphide. Methane occurs in ordinary natural waters exceptionally and in small quantity; on the other hand, many artesian waters are supersaturated with methane, so that the gas issues with the water.

The gases in natural waters can only be correctly determined if the sample is collected directly in the vessel in which the estimation is to be made, and if care is taken that the water which first enters the collecting bottle, and has therefore been in contact with air, is completely removed. Water from supply pipes is passed into the bottle for some minutes

through a narrow glass tube reaching to the bottom. To examine the water from a well provided with a pump, water is first pumped for ten minutes; the outlet pipe is then closed with a rubber stopper provided with a glass tube which also passes to the bottom of the collecting bottle. Water is then pumped through for at least five more minutes, so that a satisfactory sample is obtained In sampling running water the collecting bottle, provided with a rather wide, bent tube, is fastened to a pole and lowered into the water to the required depth (Fig. 73); a quarter of an hour should be allowed for the original contents of the bottle to be thoroughly renewed. The bottle is then lifted to the surface after the removal of the glass tube. To collect a sample of standing water, the bottle, which is fastened to a pole, is provided with a thin lead or ebonite tube to which a short glass tube is attached, and lowered to the necessary depth. The tube is then connected with a small hand-pump, and about ten times as much water as the bottle holds pumped through it. The most reliable plan is to fix a spring cap to the neck of the bottle, so that it is closed automatically after the removal of the tube. If possible, the gaseous contents should be determined at once; if this cannot be done, glass-stoppered bottles are used for collecting the sample. Care must be taken that no air-bubbles remain on closing the bottle; the stopper is covered with a piece of thin sheet rubber during transport.[1]

FIG 73

An apparatus described by R. E. Greenfield and F. L. Mickle,[2] has been found particularly convenient. The method of construction of the apparatus is clear from the accompanying diagram (Fig. 74). When the entire apparatus is immersed in water, the water enters the small bottle through the longer tube, filling the small bottle and overflowing into the larger, the air escaping through the shorter tube. This flow continues until the larger bottle is full.

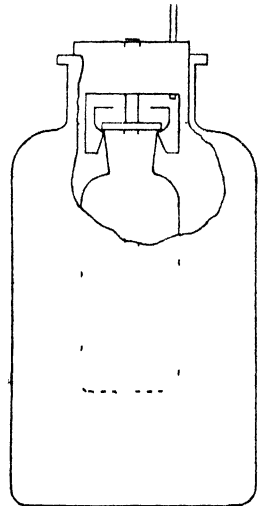



FIG. 74

[1] *Cf.* L. W. Winkler, *Z. anal. Chem*, 1901, 40, 532.

[2] State Water Survey—Annual Report for years 1918 and 1919. *Bulletin* No. 16, Urbana, Illinois, p. 197.

Glass bottles provided with glass stoppers and overlapping glass caps, both well ground, are also very suitable as collecting vessels.[1] After the bottle has been filled in the manner described above, the glass cap is also filled with the water and then placed in position.

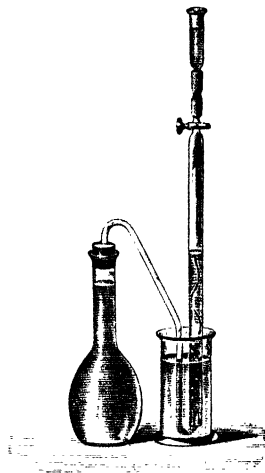
A full account of the chief methods in use for sampling river waters is given by Schumacher.[2]

The determination of free carbon dioxide has already been described (p. 411); the following methods serve for the determination of the other dissolved gases, more particularly nitrogen, oxygen, methane and hydrogen sulphide.

Nitrogen, Oxygen, Methane

The determination of dissolved oxygen and of atmospheric nitrogen (*i.e.*, nitrogen derived from air, containing argon, etc.) in natural waters is easily carried out by expelling the dissolved gases by carbon dioxide and collecting them over sodium hydroxide solution.[3] The amount of dissolved oxygen is most accurately determined iodometrically (p. 433). In gaseous mixtures expelled from water it is most easily determined by absorption with alkaline pyrogallol solution. The oxygen and nitrogen dissolved in water are expelled by carbon dioxide in the following manner:—

Fig. 75.

Ten g. of coarse-grained calcite, freed from dust by sieving, is placed in a 500 c.c. flask or bottle (Fig. 75), the capacity of which has been determined up to the stopper. A little water, acidified with hydrochloric acid, is poured on to the calcite and poured off again, after gas has been generated for one or two minutes; the object of this is merely to moisten the calcite evenly. The water under examination is then passed through the flask, in a suitable manner, for a considerable time, so as to ensure a satisfactory replacement of the initial contents. The flask is completely filled with the sample, and 20 c.c. of fuming hydrochloric acid of sp. gr. 1·18 to 1·19 quickly added from a pipette; the acid is allowed to flow into the neck of the flask, not on to the bottom. The evolution of gas does not start immediately, so that there is time to insert the rubber stopper, which is fitted with a thick-

[1] Farnsteiner-Buttenberg-Korn, *Leitfaden für die chemische Untersuchung von Abwässern*, p. 34.

[2] *Gesundheits Ingenieur*, 1904, Nos. 26, 27 and 28. Published by R. Oldenbourg, Munich.

[3] L. W. Winkler, *Z. anal. Chem.*, 1901, 40, 523.

walled gas delivery tube, into the neck of the flask, and to place the other end of the delivery tube under the measuring tube, which is filled with a 20 per cent. sodium hydroxide solution; this tube is about 40 cm. long and 1 cm. wide. The carbon dioxide, which is evolved in very small bubbles, carries the dissolved gases into the measuring tube. The operation is completed in fifteen to twenty minutes. To ensure the absorption of the carbon dioxide, the tap of the measuring tube is opened momentarily from time to time, and fresh sodium hydroxide solution admitted through the attached funnel.

The measuring tube is then transferred from the alkali solution by means of the small bottle hung on a piece of wire (Fig. 76), and placed first for a few minutes in a beaker containing distilled water, to allow the heavy liquid to diffuse out as far as possible, and then

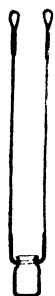
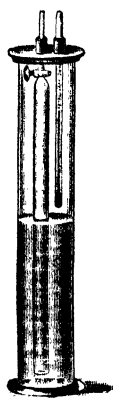



FIG. 76. FIG. 77.

in a glass cylinder, provided with a thermometer and cardboard cover (Fig. 77); water is poured into the cylinder, so that it stands 1 to 2 mm. higher than the column of liquid in the measuring tube, and the volume of gas, temperature and pressure read, after about twenty minutes.

The oxygen is determined in the mixture of oxygen and nitrogen thus obtained by the ordinary methods of gas analysis[1] (*cf.* Vol. I., p. 245).

The volume of air contained in the fuming hydrochloric acid used and the volume occupied by the calcite may be neglected in ordinary determinations. In the case of more exact measurements they must, however, be allowed for:—10 g. of calcite occupies a volume of 3·6 c.c.; from 1 litre of 38 per cent. hydrochloric acid, saturated with air at the ordinary temperature, 9·58 c.c. of nitrogen and 4.17 c.c. of oxygen were obtained on boiling, so that the correction to be deducted for

[1] *Cf.* L. W. Winkler, *Z. anal. Chem.*, 1901, 40, 529.

20 c.c. of hydrochloric acid is 0·192 c.c. of nitrogen and 0·083 c.c. of oxygen.

If the water contains considerable quantities of methane, the residual gas, after absorption of the oxygen, is inflammable. Small quantities of methane can only be detected by quantitative methods. For its estimation the gas from a separate 500 c.c. of the water is expelled with carbon dioxide as above, and collected in a small gas-holder filled with mercury containing 25 c.c. of 50 per cent. sodium hydroxide solution, to absorb the carbon dioxide. The gas thus obtained is then analysed by the usual methods (*cf.* Vol. I., p. 229 *et seq.*).

Adeney's Apparatus for the Extraction and Analysis of the Gases dissolved in Water.[1] This is a very useful form of apparatus; it has been employed in a number of important researches made in connection with the work of the Royal Commission on Sewage Disposal. It consists of a gas burette enclosed in a glass cylinder, a pressure tube, a laboratory vessel and a laboratory flask with an intermediate condenser. The way in which these parts are fitted together and supported is shown in Fig. 78.

The upper end of the burette is closed by a Friedrich's two-way stopcock, by means of which communication can be opened or closed between it and the laboratory vessel, or laboratory flask, through the two branch tubes which lead from the upper side of the stopcock. The branch to the laboratory vessel is a capillary tube, that to the flask is of 2 or 3 mm. bore. The lower portion of the burette is contracted and passes through a hole cut in the centre of a rubber bung, which closes the lower end of the glass cylinder surrounding the burette. It is then bent at right angles and connected by rubber tubing with the similarly bent end of the pressure tube. The upper contracted portion of the burette is about 225 mm. long, and has a capacity of 15 c.c.; the wider portion is about 410 mm. long, with a capacity of a little more than 250 c.c.; both portions are graduated, the former in one-tenth c.c., and the latter at intervals of 25 c.c. The pressure tube has a working length of 1000 mm. above the level of the lowest division of the burette. Its upper end is also closed by a Friedrich's stopcock. The supply of mercury to the burette and to the pressure tube is regulated by means of a reservoir, which can be moved vertically up and down at the back of the apparatus by a catgut line passing over the necessary pulleys to a windlass in front of the apparatus, as shown. The flexible tube from the reservoir is attached to a side branch fused to the lower portion of the pressure tube. The height of the mercury in the pressure tube is read by means of a millimetre scale etched on the unsilvered surface of a narrow slip of looking-glass, fixed at the back of, and close to, the

[1] *Trans. Royal Dublin Society*, New Series, 1895, Vol. V., Part XI. The editors are indebted to Dr Adeney for this description of his apparatus.

pressure tube, at an angle so as to reflect the image of the tube through the portion of the glass bearing the scale.

The laboratory vessel differs in principle and shape from that used in Frankland's and Macleod's apparatus. Its shape is shown in the figure; the lower contracted portion is 25 mm. in diameter, and 55 mm. long; it is furnished with a branch tube for connecting the vessel with a separate reservoir, which can be drawn up and down by a catgut line and a second windlass in a similar manner to that connected with the

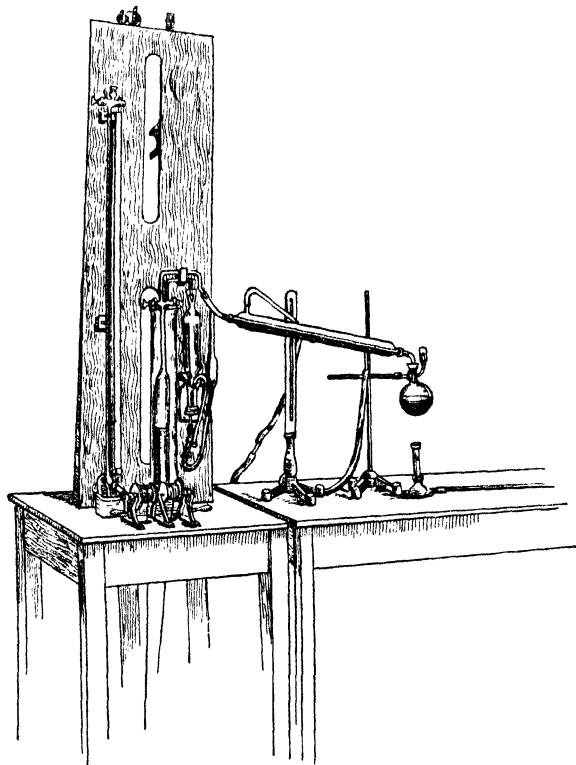



FIG. 78.

pressure tube. The middle portion is 160 mm. long, and the upper end has a funnel shape; it is 55 mm. long, and the diameter increases from 3 or 4 mm. to 20 mm. at the mouth. Two platinum wires are sealed in the sides of the vessel, for explosions. The funnel shape of the upper portion of the laboratory vessel enables it to be easily connected with, or disconnected from, the branch tube of the burette. The end of this tube is fitted with a rubber collar, and when the vessel is placed in position, the collar fits into the funnel and tightly closes it. The laboratory vessel is at the same time supported by a horseshoe-shaped shelf, as shown. If the space above the rubber collar be filled

with mercury, a perfectly air-tight joint is obtained, and a vacuum can be maintained in the vessel, or explosions may be made in it without fear of loss. To disconnect the laboratory vessel, its lower end is drawn forward sufficiently to clear the shelf, and it is then lowered to detach it from the branch tube. By reversing these movements the laboratory vessel may again be placed in position. The lower end of the vessel is closed by a rubber cork, and in order to provide the means of introducing gaseous or liquid reagents into the vessel, a glass capillary tube about 100 mm. long is fitted through the cork; the outer end of this tube is closed by a piece of capillary rubber tubing and a small screw clamp.

The method of working the apparatus is as follows:—The burette, pressure tube and laboratory vessel are filled with mercury. The laboratory flask, which has a capacity of about 1600 c.c., is fitted to the end of the condenser as shown in the figure, 50 c.c. of distilled water and generally a little sulphuric acid having previously been put into the flask. The water in the flask is then boiled, the air and steam escaping through the side tube in the neck of the flask. The boiling is continued for a few minutes, the burner then removed, and at the same time the side tube closed by a piece of rubber tubing and glass rod. The air still remaining in the flask is exhausted by working the burette and its reservoir as a Töpler pump. As air is drawn from the laboratory flask into the burette at each stroke of the reservoir, it is allowed to escape to the laboratory vessel. After the flask has been completely exhausted the vessel is disconnected from the branch tube, and a known volume of the water to be examined is drawn into the burette and then allowed to flow into the flask; the laboratory vessel is then replaced in position and reconnected with the branch tube. The water is boiled and the gases drawn into the burette and thence into the laboratory vessel for storage. After the gases have been completely extracted they are measured and analysed, the absorptions (and explosions if necessary) being carried out in the laboratory vessel.

This apparatus has been found capable of yielding extremely accurate results both for extracting dissolved gases and for their analysis. By combining the principle of the Töpler pump with the burette, and by the employment of a closed laboratory vessel with a separate mercury reservoir, the difficulties of the older forms of apparatus for extracting and analysing dissolved gases are entirely overcome.[1]

L. W. Winkler's Iodometric Method[2] is specially suitable if the dissolved oxygen only is to be determined in water. The method is based on the oxidation of manganous hydroxide to manganic hydroxide in presence of alkali by means of the oxygen dissolved in a measured quantity of the water; potassium iodide and hydrochloric

[1] *Cf.* Adeney, *Dilution Method of Sewage Disposal*, 1928. [2] *Ber.*, 1888, **21**, 2843; 1889, **22**, 1764.

acid are then added to the liquid, whereby the equivalent in iodine of the dissolved oxygen is liberated, which is titrated with sodium thiosulphate and calculated to oxygen.

The following solutions are required :—

1. *Manganous Chloride Solution.* Forty g. pure crystallised manganous chloride, $MnCl_2 \cdot 4H_2O$, is dissolved in 100 c.c. of water. The manganous chloride must be free from iron, and should separate at most only traces of iodine from an acidified solution of potassium iodide.

2. *Sodium Hydroxide Solution.* One part of pure sodium hydroxide, free from nitrite, is dissolved in 2 parts of water. About 10 per cent. of potassium iodide is dissolved in a portion of this solution for use; the mixture should not colour starch solution blue immediately after dilution and acidification with hydrochloric acid; also it should not contain much carbonate.

Fig. 79.

The estimations are carried out in thick-walled bottles of about 250 c.c. capacity, and provided with well-ground glass stoppers; the exact capacity must be known. The bottle is completely filled with the water by simply pouring it in, if the sample is saturated with air; if not, the water must be passed through the bottle until the initial contents have been fully replaced. The reagents are then introduced once by means of 1 c.c. pipettes provided with long, narrow delivery tubes which are inserted nearly to the bottom of the bottle. One c.c. of the alkaline potassium iodide solution is first introduced, followed by 1 c.c. of the manganous chloride solution; the bottle is then closed, taking care that no air-bubbles adhere, which are easily excluded by first moistening the stopper by immersion in water. The contents of the bottle are then thoroughly mixed by shaking and turning it upside down. After a few minutes the flocculent precipitate settles and the liquid in the upper part of the bottle becomes almost clear; if this clear liquid is brownish in colour, instead of colourless, the shaking is gently repeated. If the bottle is shaken for an unnecessarily long time the precipitate loses its flocculent character and becomes powdery, and then only settles slowly. If time permits, it is best to let the precipitate settle completely; in order to keep out the air, the bottle is dipped, stopper downwards, into a small beaker filled with water, and then turned upright again with the beaker. (Fig. 79). It is, however, usually sufficient to allow the bottle to stand for a few minutes. When the precipitate has settled so that the liquid in the upper part of the bottle is clear, the stopper is removed and about 5 c.c. of fuming

hydrochloric acid added by a pipette with a long delivery tube previously moistened with water. The bottle is then again closed and the contents mixed; the precipitate quickly dissolves and a liquid coloured yellow by iodine is obtained; this is titrated with an *N*/100 sodium thiosulphate solution in the usual manner; each c.c. of this corresponds to 0·055987 c.c. oxygen at 0° and 760 mm.

No correction is made in the method, as described, for the quantity of dissolved oxygen in the reagents, but as the total volume of the latter is approximately only 1 per cent. of the total liquid, the error from this source is practically negligible. For standard determinations air-free reagents must be used and the hydrochloric acid must be freed from all traces of air by treatment with carbon dioxide.[1]

As manganous carbonate is not oxidised by oxygen, a double quantity of sodium hydroxide solution, that is, 2 c.c., must be used for waters containing considerable quantities of carbon dioxide.

Dissolved oxygen can be very accurately determined in pure natural waters by this method. If, however, the water contains considerable quantities of organic matter, this may combine with some of the iodine, so that less oxygen is then found than is really present. To avoid this source of error, 100 c.c. of distilled water and 100 c.c. of the water to be examined are each treated with 10 c.c. of *N*/100 iodine solution, and the amount of iodine remaining in each liquid titrated with *N*/100 sodium thiosulphate solution after a few minutes. The difference in the amount of thiosulphate solution used in the two cases gives the value of the correction per 100 c.c. of the water.

The presence of nitrous acid in a water, even to the extent of 0·1 mg. per litre, interferes seriously with the reliability of the method. Nitrous acid liberates iodine from the acidified potassium iodide solution, but the quantity of iodine formed in this way is usually negligibly small; the serious interference with the reaction is caused by the nitric oxide formed from the nitrous acid, which acts as an oxygen carrier in much the same way as in the ordinary sulphuric acid process, causing a continuous absorption of oxygen from the air, during the titration.

Rideal and Stewart,[2] in using Winkler's iodometric method for the estimation of dissolved oxygen in water, recommend first oxidising the organic matter and nitrites present by means of an *N*/10 potassium permanganate solution and concentrated sulphuric acid. The quantity of permanganate solution required is first determined by a preliminary test, and any slight excess used in the actual determination destroyed by the addition of a solution of neutral potassium oxalate.

Experiments by Fowler have shown that in presence of much oxidisable matter it is preferable to destroy the nitrites by the addition of urea, in acid solution.

[1] *Cf.* L. W. Winkler, *Ber.*, 1889, **22**, 1764.

[2] *Analyst*, 1901, **26**, 141.

Winkler[1] suggests the use of chlorine as calcium hypochlorite for destroying nitrites and organic matter. The method gives good results, but an additional titration is required to determine the excess of chlorine added.

Phenosafranine Method. For rapid field work Miller[2] has suggested a method based on the reduction of phenosafranine by ferrous salts. This method has been found useful in practice, the details being as follows:—

To 50 c.c. of the water contained in a 100 c.c. Nessler cylinder is added 5 c.c. of alkaline tartrate such as is used for Fehling's solution and one drop of phenosafranine solution (1 in 2000 of water), then from a 10 c.c. pipette a solution of ferrous sulphate (0·22 g. of pure $FeSO_4$ and 1 c.c. of concentrated sulphuric acid in 100 c.c.) is run in just below the surface of the liquid, stirring gently with the pipette until the colour is discharged, looking through the cylinder horizontally. The ferrous sulphate is added 1 c.c. at a time until the colour begins to fade, then in portions of 0·5 c.c. to the end. There is a slight coloration at the surface of the liquid, but if the stirring is not too vigorous this does not interfere. The outlet hole of the pipette should not be more than 1 mm. in diameter to minimise diffusion.

Ferrous Sulphate—Permanganate Method. In the prolonged investigations of the waters of New York Harbour undertaken by the Metropolitan Sewerage Commission of New York, during the period 1909-1914, and continued since by Kenneth Allen, Sanitary Engineer to the Board of Estimate and Apportionment of the City of New York, the Albert-Levy method was adopted, akin to that employed by Letts and Adeney in their estuarial studies. This method depends on the absorption of oxygen by ferrous sulphate in the presence of an alkali, the amount of ferrous sulphate not acted upon by the oxygen being then determined by acidifying and titrating with potassium permanganate. The details of this method were the subject of very careful criticism by a Committee of Experts.

The reagents used are as follows:—

Standard Ferrous Sulphate. This is prepared by dissolving 144 g. of Kahlbaum's crystallised ferrous sulphate in water, adding 15 c.c. of concentrated sulphuric acid and diluting the whole to 3 litres.

Standard Sodium Carbonate. Prepared by dissolving 200 g. of sodium carbonate crystals in 1 litre of water.

Standard Sulphuric Acid. Prepared by mixing equal parts of concentrated sulphuric acid and water.

Standard Potassium Permanganate. Prepared by dissolving 25·4 g. of potassium permanganate in water and diluting to 4·5 litres. This reagent is standardised against specially prepared Mohr's salt.

[1] *Z. angew. Chem.*, 1916, **29**, 44. *Analyst*, April 1916.
[2] *J. Soc. Chem. Ind.*, 1914, **33**, 185.

The determinations are made in a bottle known as the Soper Ogygen Bottle, from having been devised by the President of the Commission. It is shown in Fig. 80. The bottle is usually of about 500 c.c. capacity, with a long funnel-shaped lip. A stopper which is convex at the bottom fits accurately into the neck, and when in place permits about 15 c.c. of liquid to stand in the funnel without overflowing. The capacity of the bottle is accurately determined with the stopper in place. The purpose of this apparatus is to permit of the addition of reagents to the bottle without exposing the contents to air.

In use the bottle is filled to the beginning of the funnel with the water to be examined and the stopper is set down in place. The excess of water which rises in the funnel is poured off. The stopper is removed and to the bottle of about 500 c.c. capacity, 6 c.c. of the standard solution of ferrous sulphate is delivered by a pipette to the bottom of the bottle, where it remains unless the bottle is agitated. The stopper is replaced and the water which rises in the funnel is poured off. Five c.c. of sodium carbonate solution (200 g. per litre of water) is then poured into the funnel. The stopper is cautiously raised sufficiently to allow the heavy alkali to sink through the water to the bottom of the bottle, where the reaction producing a heavy precipitate begins. The stopper is put back in place, the water in the funnel is poured off and the bottle is shaken until the free oxygen is entirely absorbed. Ten c.c. of a 50 per cent. solution of sulphuric acid is poured into the funnel and the stopper raised sufficiently to permit the heavy acid to diffuse, discolouring and permitting the contents of the bottle to be titrated. Finally, the contents are poured into an Erlenmeyer flask and titrated with permanganate of potash, each c.c. of which represents 1 c.c. of oxygen.

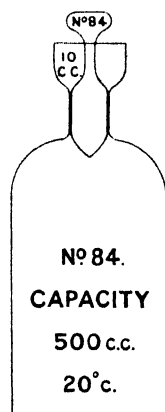



Fig. 80.

A blank determination is made whenever the water contains much organic matter or sodium chloride. The same steps are followed in making the blank as in making the analysis except that the sodium carbonate is omitted. The difference between the permanganate required by the blank and that absorbed in the actual analysis represents the dissolved oxygen present.[1]

By means of oxygen determinations the "oxygen demand" of the water may also be investigated. For this purpose, air, filtered through cotton-wool, is passed for fifteen minutes through 1 to 2 litres of the water to be examined, in order to saturate it with air; it is then divided into calibrated bottles, which are closed with stoppers and inverted beakers filled with water, as described above. If the water originally

[1] *Report of the Metropolitan Sewerage Commission of New York*, 1914, p. 608.

contains much oxygen, it is unnecessary to pass air through. In one of the bottles the dissolved oxygen is at once determined; the others are kept in a dark place at the ordinary temperature, and the dissolved oxygen determined after standing for successive intervals of time, such as after one day, a few days, a week, etc. In an impure water a diminution of the oxygen occurs as part of it is used up, in oxidising the organic matter in the water with the help of micro-organisms. The greater this diminution, the greater the oxygen demand of the water. In pure, natural waters the diminution is so small that it can scarcely be measured; in waters containing much organic impurity and rich in bacteria it is appreciable, and in sewage water it is considerable. In this case it is more satisfactory to dilute the sample, say, ten times with well aerated tap water and determine the progressive loss of oxygen in the mixture.

In some waters, after exposure to sunlight, an increase in the oxygen may be observed; this is due to the presence of microscopic aquatic plants containing chlorophyll, which by their metabolism liberate oxygen from carbon dioxide.

The results by Adeney[1] illustrate the value of the determination of the dissolved gases in water (see Tables I. and II. below).

I.—Samples of Water from the River Liffey, just above the Weir at Island Bridge, Dublin.

The dissolved gases expressed as volumes at N.T.P. per 1000 volumes of water; the other constituents as parts per 100,000.

Description of Samples.	Dissolved Gases.			Nitrogen as:—		Cl_2.
	CO_2.	O_2.	N_2.	NH_3.	N_2O_5.	
Sample slightly turbid, yellowish-green tint; traces of suspended matter .	58·78	5·25	14·34	·0040	·034	1·26
The same after keeping in closed vessel for thirty-seven days . .	62·13	0·88	14·25	·0015	·0385	...
Slightly turbid, brown colour; traces of suspended matter . . .	41·38	7·49	15·55	·004	·027	1·21
The same after fifteen days . .	42·12	6·54	15·45	·004	·035	...
Distinctly turbid, olive green tint; small quantity of vegetable débris in suspension	43·47	5·98	15·52	·002	·026	1·26
The same after fifteen days . .	48·61	1·06	15·38	·035	·011	...
Turbid, yellowish-green tint; traces of suspended matter; collected during heavy rain after dry weather .	72·64	3·23	14·93	·0028	·051	1·4
The same after eight days . .	75·62	0·44	14·99	·023	·035	...

[1] *Loc. cit.*

II.—Samples of Well-Waters.

The dissolved gases expressed as volumes at N.T.P. per 1000 volumes of water; the other constituents as parts per 100,000.

Description of Samples.	Dissolved Gases.			Nitrogen as:—		Cl_2.
	CO_2.	O_2.	N_2.	NH_3.	N_2O_5.	
Sample clear and colourless, with minute traces of suspended matter	205·10	5·64	14·83	·002	·12	3·5
The same after thirty-four days .	204·72	5·32	14·70	·000	...	...
Sample slightly turbid, colourless, and free from suspended matter . .	113·69	4·03	15·69	·016	·254	5·9
The same after twenty-one days .	113·54	3·76	15·78	·000	...	...

The oxygen demand of a water can be expressed in degrees, as the number of c.c. of dissolved oxygen per 100 c.c. of dissolved oxygen originally present, which disappear during the first twenty-four hours.

For purposes of comparison, the solubility of atmospheric air and of oxygen and nitrogen in water at various temperatures, is given in the table on p. 440.

The data, which include determinations by L. W. Winkler,[1] give the volumes of the gases in air, free from carbon dioxide and ammonia, reduced to normal temperature and pressure, which saturate 1000 c.c. of water at 760 mm. pressure.

Under the same conditions 1000 c.c. of water dissolves the following volumes of methane:—

Temp.	c.c.	Temp.	c.c.
0°	55·30	20°	32·33
5°	47·64	25°	29·13
10°	41·27	30°	26·48
15°	36·28		

The whole subject of the oxygen demand of polluted waters is dealt with exhaustively by C. E. J. Theriault in Bulletin No. 173 of the U.S. Public Health Service. The details of the dissolved oxygen determination, by the Rideal-Stewart modification of the Winkler method, are given in Bulletin No. 151 of the same service.

Hydrogen Sulphide

Hydrogen sulphide occurs in some ground waters, but usually in such small amount that it is best determined colorimetrically, rather than by the iodometric method proposed by Dupasquier and Fresenius.[2]

If water containing hydrogen sulphide is treated with Rochelle salt solution (to prevent the precipitation of calcium and magnesium

[1] *Ber.*, 1901, 34, 1419.

[2] *Cf.* Fresenius, *Quantitative Analysis*, 7th ed., 1876, vol. i., p. 381; also, Tiemann-Gärtner, *loc. cit.*, p. 227.

carbonate) and an alkaline solution of a lead salt, it is coloured more or less brownish, according to the amount of hydrogen sulphide present. By comparing the coloration with that given by a dilute sulphide solution of known strength, the quantity of hydrogen sulphide present in the water can be estimated. As a standard solution, L. W. Winkler[1] recommends an ammoniacal solution of arsenic trisulphide of such concentration that 1 c.c. corresponds to 0·1 c.c. of hydrogen sulphide gas at 0° and 760 mm. pressure.

Solubility of Oxygen, Nitrogen, and Air in Water at 760 mm.

Temperature.	Oxygen. c.c.	Nitrogen, Argon, etc. c.c.	Total. c.c.	Percentage of Oxygen in the Dissolved Air.
0	10·19	18·99	29·18	34·91
1	9·91	18·51	28·42	34·87
2	9·64	18·05	27·69	34·82
3	9·39	17·60	26·99	34·78
4	9·14	17·18	26·32	34·74
5	8·91	16·77	25·68	34·69
6	8·68	16·38	25·06	34·65
7	8·47	16·00	24·47	34·60
8	8·26	15·64	23·90	34·56
9	8·06	15·30	23·36	34·52
10	7·87	14·97	22·84	34·47
11	7·69	14·65	22·34	34·43
12	7·52	14·35	21·87	34·38
13	7·35	14·06	21·41	34·34
14	7·19	13·78	20·97	34·30
15	7·04	13·51	20·55	34·25
16	6·89	13·25	20·14	34·21
17	6·75	13·00	19·75	34·17
18	6·61	12·77	19·38	34·12
19	6·48	12·54	19·02	34·08
20	6·36	12·32	18·68	34·03
21	6·23	12·11	18·34	33·99
22	6·11	11·90	18·01	33·95
23	6·00	11·69	17·69	33·90
24	5·89	11·49	17·38	33·86
25	5·78	11·30	17·08	33·82
26	5·67	11·12	16·79	33·77
27	5·56	10·94	16·50	33·73
28	5·46	10·75	16·21	33·68
29	5·36	10·56	15·92	33·64
30	5·26	10·38	15·64	33·60

For the estimation of small amounts of hydrogen sulphide in natural waters the following solutions are needed:—

1. Twenty-five g. of crystalline Rochelle salt, 5 g. of sodium hydroxide and 1 g. of lead acetate are dissolved in 100 c.c. of water.

2. 0·0367 g. of pure, dry arsenic trisulphide is dissolved in a few drops of ammonia and the liquid diluted to 100 c.c.; 1 c.c. of this

[1] *Z. anal. Chem.*, 1901, 40, 772.

solution corresponds to 0·1 c.c. of hydrogen sulphide gas at 0° and 760 mm. pressure. The arsenic trisulphide is prepared by adding a solution of 1 g. of arsenic trioxide in dilute hydrochloric acid to 100 c.c. of freshly prepared hydrogen sulphide water and drying the precipitate at 100°, after washing. The ammoniacal solution does not keep, and is therefore prepared as required for use.

The estimation is carried out as follows:—One hunded c.c. of the water to be examined is poured into a colourless glass bottle of about 150 c.c. capacity in which 5 c.c. of reagent No. 1 has previously been placed. One hundred c.c. of distilled water and 5 c.c. of the reagent are treated in a similar bottle with the ammonium thioarsenite solution, which is added from a small, narrow burette, until the colorations in the two bottles are equal. The number of c.c. of ammonium thioarsenite solution used is equal to the number of c.c. of hydrogen sulphide contained in a litre of the water.

If a more exact determination is required, the water is passed through a stoppered bottle of rather more than 100 c.c. capacity, at the source of supply, until the initial contents of the collecting bottle have been thoroughly replaced, the bottle completely filled, 5 c.c. of reagent No. 1 run into the bottom of the liquid from a long narrow pipette, the bottle closed and the contents thoroughly mixed. The hydrogen sulphide is then estimated in 100 c.c. of the liquid, using 95 c.c. of distilled water and 5 c c. of the reagent for comparison. The hydrogen sulphide content of the original water is then obtained by calculating the amount found in 100 c.c. of the sample.

This method has the advantage that the results are not affected by the presence of thiosulphates, which are usually contained in sulphuretted waters. If less than 0·2 c.c. of hydrogen sulphide per litre is present, from 500 to 1000 c.c. of the sample is taken for the estimation; if more than 1·5 c.c. per litre is present the coloration is too great, and it is then best to employ the iodometric method of Dupasquier and Fresenius.

If the water containing hydrogen sulphide is coloured, neither the colorimetric nor the iodometric method can be used. The hydrogen sulphide must then be expelled by means of carbon dioxide generated in the liquid, and the gaseous mixture passed through bromine water, which oxidises the hydrogen sulphide to sulphuric acid. The estimation is carried out as in the determination of the total carbon dioxide (p. 411), 20 g. of coarsely granular calcite, which does not give off any hydrogen sulphide on treatment with acid, being used instead of metallic zinc; the volume of this weight of calcite is =7·2 c.c. A collecting bottle of 500 c.c. capacity is used, in which it is best to place the calcite before collecting the water. For the estimation, the glass vessel *b* (Fig. 72, p. 411) is placed in position, connected with a small

wash-bottle containing dilute bromine water free from sulphuric acid and 50 c.c. of concentrated hydrochloric acid is then gradually added through the dropping funnel. After the evolution of gas has ceased the bromine water is evaporated to a small bulk and the sulphuric acid formed is determined gravimetrically.

Microscopic Examination.

The object of the microscopic examination of water is to determine whether direct pollution has occurred either by means of polluted feeders or of insufficient earth filtration, or by the introduction of fæces, domestic refuse, or similar impurities. Such water, in addition to being offensive, often contains pathogenic germs, and must, of course, be rejected, both as a drinking water and as a supply water for domestic purposes.

The microscopic examination is carried out by observing the sediment with a magnification of from 50 to 500. If the water is perceptibly turbid it is allowed to settle in the collecting bottle for twenty-four hours. A little of the sediment is then removed by closing the upper end of a glass tube with the finger, immersing it quickly to the bottom of the bottle and opening it so that a little of the sediment enters; the tube is then closed again with the finger, carefully removed from the bottle and a small drop of the contents placed on the object glass and covered with a cover glass. If the water is not noticeably turbid it is first allowed to settle in the collecting bottle, the larger part carefully decanted off and the remainder poured into a conical test-glass; after standing overnight, a sample of the deposit is taken from the bottom of the glass as described.

The sediment from an unpolluted water consists mainly of mineral fragments. Green algæ and infusoria also often occur.

Where there is gross pollution, microscopic particles of undigested food and other intestinal debris may be discovered.

More usually it will be necessary carefully to examine any growth or deposit in the stream, well, or cistern from which the water sample may be taken. In addition to mineral fragments various species of micro-flora and infusoria may be observed which vary according to the state of purity of the water. A careful study of such growths may often lead to the discovery of sources of pollution unrevealed by chemical analysis.

Further details concerning the microscopic examinations of water will be found in the following more special works:—

Tiemann-Gärtner, *Untersuchung und Beurteilung der Wässer;* C. Mez, *Mikroscopische Wasser-Analyse;* Thresh and Beale, *The Examination of Water and Water Supplies;* G. C. Whipple, *The Microscopy of Drinking Water.* (See Literature, p. 453.)

BACTERIOLOGICAL EXAMINATION.

The purpose of the bacteriological examination is to determine the number of living bacteria and bacterial spores present in the water, and more especially to determine the presence or otherwise of sewage pollution. The actual isolation of specific water-borne pathogenic organisms such as typhoid or cholera is a task for the bacteriological expert.

The bacteriological methods for the detection of probable sewage pollution are now so well known and systematised that they may generally be undertaken by a chemist who has undergone the necessary training in bacteriological technique. Such an examination will usually suffice to show whether there is ground for suspicion of pollution or otherwise and should always be preceded or followed by a careful inspection of the source of supply.

The bacteriological indications of sewage pollution may be briefly summarised as follows:—

1. Large number of organisms growing on nutrient gelatine at 20° and especially a large proportion of liquefying organisms.
2. Large number of organisms growing on nutrient agar at 35°.
3. Presence of organisms producing acid and gas in media containing peptone and sodium taurocholate together with lactose and glucose respectively.
4. Presence of sporing organisms capable of clotting milk.

The sample for the bacteriological examination should be taken with special care and be collected in a small, glass-stoppered bottle. The bottle is first sterilised by a prolonged heating in an air-bath at 150°, opened only just before collecting the sample, and closed immediately afterwards. If the sample is collected from the main the water must first be allowed to run for some time; similarly, the water from a well provided with a pump, should be pumped through for about ten minutes. Samples of spring water or of surface water are taken with a bottle fastened to a wire, which is filled by simple immersion. It is most important to remember that the bacteriological contents of a water may increase considerably on standing for even less than a day, and any delay should therefore be avoided in making the examination. This change may be minimised though not entirely prevented by enclosing the bottle in a suitable tin and packing it in ice.

A single bacteriological examination is seldom sufficient for any definite view to be formed as to the character of a water supply; a series of tests are really necessary, which should be made at suitable intervals, such as in summer and winter, before and after a rainy period at high and low water, etc.

In the following paragraphs are described the preparation and use of the nutrient media required for the general characterisation of the bacterial contents of a water supply.

Preparation of Nutrient Gelatine.—Twenty g. (22 g. in summer) of finest, dry gelatine, cut into small pieces, is placed in a flask, 200 c.c. of distilled water added, and the whole warmed on the water-bath, with thorough shaking, until complete solution takes place. This gelatine solution is then clarified by the addition of 10 c.c. of a solution of fresh white of egg mixed with an equal volume of distilled water. The liquid is then warmed on the water-bath until the albumin has coagulated in flakes, the solution poured through a large, pleated filter-paper, and the filtrate, which is at first turbid, poured back on to the filter until it comes through clear; the whole is then placed in a drying-oven at about 40°. The filtration takes about two hours. The filtrate which is somewhat acid, is treated with sodium hydroxide solution till sensitive blue litmus paper is just reddened; if too much alkali is added the solution becomes turbid after a short time.

Nutrient gelatine prepared in this way is quite suitable for the examination of water when it is only necessary to decide whether the sample is poor or rich in bacteria. It has been shown by parallel experiments that the addition of meat-extract, peptone and salt, etc., for this purpose, is quite unnecessary.

For comparison with results on nutrient agar, however, a medium is used made up in the following proportions :—

Liebig's Meat Extract	9 g.
Witte's Peptone	9 g.
Sodium Chloride	4·5 g.
Distilled Water	900 g.
Gelatine	100 g. (150—180 g. in a hot climate)

The meat extract, peptone, salt and water are boiled for a quarter of an hour and the gelatine gradually added as it dissolves. The whole is allowed to cool (to 50° approx.) and neutralised with about 30° c.c. of a 4 per cent. solution of caustic soda (NaOH). The white of an egg is mixed with an equal volume of water and added to the neutralised liquid. The mixture is placed in the steam-bath for one hour and 1·5 g. sodium carbonate crystals added.

After a further forty minutes in the steam-bath the liquid is filtered hot as described.

When finished, about 10 c.c. of the nutrient gelatine is poured, whilst still warm, into each of a number of test-tubes, care being taken in introducing the nutrient gelatine that the upper part of the test-tube remains clean; the most convenient and cleanest method is to use a stopcock burette for this purpose. The test-tubes are then carefully

closed with cotton-wool and placed in a wire basket to which a wire handle is attached, for sterilisation; the basket is lowered into a large cylindrical container of tinned iron sheeting, or of copper, with a false perforated bottom, below which a layer of water an inch or two in depth is placed. A dome-shaped cover is then placed over the container and the whole heated; the water is boiled vigorously for fifteen minutes from the time the steam begins to escape. The object of the sterilisation is to kill any bacteria, either contained in the gelatine or adhering to the cotton-wool or to the sides of the test-tubes. As, however, a single sterilisation at 100° does not infallibly destroy the spores of micro-organisms, the sterilisation is repeated on each of the two following days. The test-tubes containing the sterile gelatine are kept in a tin in a cool place; they will remain unchanged for months, as the cotton-wool plug prevents the entry of bacteria from the atmosphere. If the sterilisation has not been carried out with sufficient care colonies of bacteria may develop; such tubes must, of course, be discarded.

It is now customary in most laboratories to adjust the reaction of the medium to a definite hydrogen-ion concentration (see p. 388). For this purpose, special indicators, such as phenol red (pH = 6·8-8·4), or bromthymol blue (pH = 6·0-7·6) are used, and the titration made with 5 c.c. of the medium diluted with 5 c.c. of water in small tubes mounted for convenience of observation in a "comparator," formed from a block of wood suitably pierced with cylindrical holes to contain the tubes, and blackened to prevent reflection of light.[1]

Agar Medium.—For cultures to be grown at a high temperature, *agar agar*, a Japanese product made from a species of marine alga, is used instead of gelatine in the above process, 30 g. only being taken instead of 100 g. as with gelatine. In order to filter the medium rapidly it is convenient if practicable to heat the whole filtering arrangement to slightly over 100° in a large autoclave.

Bile Salt Medium.—This medium is used especially for the detection of bacteria capable of fermenting certain sugars with production of acid and gas. These belong to the type known as *Bacillus coli communis*, and are characteristic of sewage pollution.

The base of the medium is a concentrated solution of the following composition:—

Peptone	60 g.
Sodium taurocholate	15 g.
Neutral red or litmus	a sufficiency.
Water distilled	1 litre.

From this solution media can be prepared each containing in addition 15 g. of a specific sugar. For routine purposes only glucose

[1] Sold by British Drug Houses, Ltd., Graham Street, City Road, London.

and lactose are as a rule employed. For special research, saccharose, dulcite and adonite are also made use of, the character of the pollution being judged by the particular sugar fermented.

In bile salt media, it is important that all dilutions should be as far as possible of the same strength, viz., containing about one-third by volume of the concentrated solution. When the volume of water to be examined is 10 c.c. or less, it is convenient to dilute the concentrated solution once for all to various strengths according to the volume of the water to be examined so that 10 c.c. of the medium may be used in each case.

Such dilutions are as follows:—

(*a*) for 10 c.c. of water—

concentrated solution	200 c.c.
distilled water	100 „

(*b*) for 5 c.c. of water—

concentrated solution	150 c.c.
distilled water	150 „

(*c*) for 2 c.c. or smaller quantities of water—

concentrated solution	100 c.c.
distilled water	200 „

A number of test-tubes, 6 in. long and ¾ in. wide, are thoroughly cleaned, and into each is inserted a small inverted test-tube (1½ in. × ¼ in.) in which any gas evolved may be observed.

Into each of the required number of these tubes 10 c.c. of the medium either (*a*) (*b*) or (*c*) is placed and the tubes are plugged and sterilised.

Milk Medium.—This medium is used for the detection of the sporing organism *Bacillus enteridititis sporogenes*, which is characteristic of sewage pollution. Skimmed milk is used, one volume of which may be diluted with two volumes of the water to be tested.

Conical flasks may conveniently be employed for quantities above 20 c.c. of the water. The milk should be boiled immediately before use, and the water added as soon as the milk has slightly cooled. As the organism to be looked for is anaërobic, air is excluded from the milk by running a film of melted vaseline (mixed with a little paraffin) over the surface with a pipette, to a depth of about half an inch.

The tubes or flasks are heated in a water-bath at 80° for fifteen minutes to destroy all adult bacteria, leaving any spores intact. They are then placed in cold water to allow the vaseline to set and afterwards incubated at 37° for some days. If spores of *Bacillus enteriditis* are present, clotting and gas formation take place.

Counting the Bacteria.—The bacteria developing in solid media are grown in "Petri dishes," which are made of glass. The clean, covered dishes are first sterilised by heating to 150° to 160° for one

hour in an air-bath, by which means adherent bacteria and spores are destroyed; after cooling they remain sterilised inside as long as they are kept covered. If special dishes are not available, ordinary crystallising dishes of about 10 cm. diameter, or conical Erlenmeyer flasks (Cramer) may be substituted, somewhat larger crystallising dishes being used as a cover for the former.

To take the sample of water to be examined, a glass tube, 15 to 20 cm. long and of about 5 mm. diameter, is drawn out at the end to a thin point so as to form a pipette; the thin end of the pipette is bent at an obtuse angle, the extreme end sealed in a flame before sterilising, and the wide end closed with a plug of cotton-wool. The pipette is then sterilised in the same way as the dishes.

The bacteriological examination should always be made either on the spot, or with the freshly collected sample. To take the sample, the point of the pipette is broken off, passed several times through a flame, to destroy any adhering bacteria, and then dipped into the sample; when 1 to 2 c.c. of the water have entered, the pipette is withdrawn and the water introduced into the sterilised culture dishes; one drop is placed in the first dish, five in the second, and ten in the third, the dishes being half-opened for this purpose, and then closed again at once.

The water is then mixed with the sterilised gelatine. The gelatine is first liquefied by placing the test-tubes in water warmed to 40°, the melting-point of the 10 per cent. nutrient gelatine being 32°; after it is completely melted the cotton-wool plug is removed, the open end of the test-tube held for a moment in the flame to destroy any adhering bacteria and the gelatine poured into the dish; care must, of course, be taken that the dishes are only opened for a very short time, to avoid the admission of bacteria from the air. The gelatine and water are then carefully mixed by moving the covered dish round in such a way that the liquid on the bottom acquires a circular motion. The number of drops of water added to each dish is noted on the lid and the dishes then placed on a horizontal plate, when the contents soon gelatinise. The volume of a drop delivered by the pipette is determined by counting the number of drops in 1 c.c.; if, for instance, there are forty drops per c.c., the volume of each drop is 0·025 c.c., and therefore the first dish contains 0·025 c.c., the second 0·125 c.c., and the third 0·250 c.c. of the water. After the contents of the dishes have set, they are kept at the ordinary temperature; they must not be exposed to direct sunlight.

The same procedure is carried out with nutrient agar; care, however, must be taken to heat the medium to such a temperature that it is not too hot to kill the bacteria and not so cool as to set too quickly on pouring into the Petri dish and so prevent a uniform mixture being made with the sample to be tested.

After twenty-four to forty-eight hours little spots can usually be seen in the crystal-clear layer of gelatine; these are the bacteria colonies. If possible, one to two days are allowed to elapse so that the colonies may develop, before they are counted. If too long a time is allowed, the gelatine usually liquefies, or the colonies of mould fungi grow so rapidly that they cover the others. The dish, the contents of which appear the most suitable, is selected for counting the colonies. If the colonies are sparsely scattered in the dish they are all counted; for this purpose the dishes are inverted. In order to avoid error in counting, the positions of colonies already counted are marked in ink on the outside of the glass. If the colonies are closer together, the bottom of the dish is divided radially into fields with pen and ink or with a glass-pencil, and the colonies counted separately in each field. If very many colonies have formed in the culture, they must not be allowed to grow large, but must be counted comparatively soon, with the help either of a simple lens or a "thread-counter," which has an opening of 1 sq. cm. in the lower plate. The dish is inverted over a piece of black paper, and the number of colonies in 1 sq. cm. of several parts of the bottom of the dish counted; the total number of colonies is then computed from the mean of the number found in the sections examined. Thus, suppose that in the third dish, which contained ten drops = 0·25 c.c. of the water, sixteen colonies, on the average, had developed per sq. cm., and that the diameter of the dish was 10 cm., the area of the bottom, πr^2, = 78 sq. cm., and the total number of colonies = 16 × 78 = 1248; therefore 1 c.c. of the water contains 4 × 1248, or approximately 5000 bacteria and spores.

As a check on the determination, it is advisable to conduct a parallel experiment with the nutrient gelatine by itself; if the examination has been properly carried out, either no colonies at all or only very few should develop in this dish; should any form, the number must of course be proportionately deducted from those formed from the water.

In liquid media the number of bacteria present cannot be directly counted. It is sufficient, however, to determine the volume of water in which a positive reaction is given. The limits above or below which a water may be considered safe on the one hand or dangerously polluted on the other cannot be absolutely defined and must always be considered in relation to local conditions, but it may be safely stated that if coli-like organisms are absent in 100 c.c. the water is likely to be of first-rate quality, while if they are present in 1 c.c. the water is potentially dangerous.

Much work has been done of recent years with the object of distinguishing between recent and past pollution, and there is evidence to indicate that a recently polluted water will show the presence of lactose and glucose fermenters in equal volumes, while such a water

on keeping will show fewer lactose than glucose fermenters. A water therefore in which more glucose fermenters can be detected than lactose fermenters may be considered less dangerous than a water in which both types of organism are present to an equal extent.

For further details on the bacteriological examination of water, the following works may be consulted:—Tiemann-Gärtner, *Untersuchung und Beurteilung der Wässer;* P. F. and G. C. Frankland, *Micro-Organisms in Water;* David Ellis, *Practical Bacteriology for Chemical Students;* W. H. Horrock, *Introduction to the Bacteriological Examination of Water;* Thresh and Beale, *The Examination of Waters and Water Supplies;* W. W. Clemesha, *The Bacteriology of Surface Waters in the Tropics;* Muir and Ritchie, *A Manual of Bacteriology;* A. C. Houston, *Studies in Water Supply.* See also *Reports of Metropolitan Water Board,* by Sir A. Houston.

INTERPRETATION OF RESULTS

Rain water is seldom used as a drinking water, both on account of its insipid taste and of its liability to contamination; when used, in default of a better source of supply, the surface from which it is collected and the storage-tanks or cisterns should be kept as clean as possible.

Drinking water is usually ground water; spring water is the best drinking water, and a pure well supply is also good. Both spring water and well water can be regarded as satisfactory from a hygienic standpoint, provided the spring is properly lined and covered, and the well is of the necessary depth, the adjoining soil free from pollution, and that impurities cannot be extraneously introduced either by falling in or by flowing in, or contamination occur through inefficient earth-filtration from closets, cesspools, sewers, dung-heaps, stables, etc., in the vicinity. A well in a densely populated district will, however, seldom comply with these conditions. The water of artesian wells is very good drinking water if drawn from a sufficient depth and from a good substratum; it should then be clear, colourless or nearly so, and of pleasant taste, as extraneous impurities are hardly likely to occur.

Unfiltered, stagnant, or surface water (water from ponds, rivers, etc.) is unsuitable for drinking or domestic purposes, as dangerous and possibly infectious impurities may easily be introduced. If, however, such water is purified by suitable filtration beds, it may be quite safe for use, unless subsequently contaminated, for instance, by lead introduced from the service pipes.

The criteria for the hygienic valuation of a water are based upon: 1. An examination of the local conditions of supply; 2, The results of the physical, chemical, microscopic and bacteriological examinations. In exceptional cases the one or other method of investigation may alone

suffice, but usually both local inspection and the data derived from all the other methods of examination must be considered in judging the suitability of a water from a hygienic standpoint. The following are the chief points which come under consideration in the valuation of a water supply:—

1. A careful local inspection of the conditions of supply is essential, and the geological character of the district should also be examined.

2. If the water is colourless, crystal clear, odourless, and has a pleasant, refreshing taste, it is quite satisfactory; such water is supplied by well-kept springs and by good wells. In water from artesian wells a coloration is of minor importance. A spring or well water which is turbid is always suspicious, but much depends on the cause of the turbidity. If it is due to very finely-divided clay or other mineral debris, it is not dangerous to health, but is unpalatable; if, however, the turbidity is caused by impurities introduced into the water, it must be absolutely condemned for drinking or domestic purposes, as offensive and as a most probable source of infection. Water which is unpleasant to the smell or taste should not be used as drinking water; a slight smell of hydrogen sulphide, particularly if it soon disappears on standing in the air, may be admitted in the case of artesian well waters. Water which is poor in bicarbonates or in free carbon dioxide is not unwholesome, but is lacking in freshness to the taste.

3. Drinking water should be cool, but not ice-cold. The consumption of ice-cold water may be injurious to health; water at above 15° is not palatable. In general, the temperature of a spring or well water should only vary slightly from the mean temperature of the locality, and therefore but little during the different seasons of the year.

4. The residue on evaporation from 1 litre of water should not exceed 500 mg.; any greater proportion can only be regarded as unimportant if conditioned by the geological nature of the district.

5. Water of medium hardness (18° to 25°) is the most suitable for drinking water. Very hard water may cause temporary intestinal disturbance to those not accustomed to it; 60° of hardness may be considered as the ordinary limit for drinking water. Distilled water, glacier water, and rain water are almost undrinkable owing to their lack of hardness.

Hard water is unsuitable for domestic purposes. Vegetables, especially peas and beans, cannot be thoroughly cooked in hard water, and in laundry work, washing, etc., an excessive quantity of soap is used up.

For most technical purposes, especially for boiler-feed water, soft water is desirable; many of the fermentation industries, as well as tanneries, laundries, etc., also require soft water (*cf.* pp. 454-460).

If a well water is notably harder than the normal water of the

district, this is often an indication of the decay of organic matter in the soil, which gives rise to the formation of carbon dioxide and nitric acid, which exert a solvent action on the minerals of the soil.

6. The quantity of chlorine in drinking water is usually small, being generally milligrams and seldom centigrams per litre. If the water rises in the neighbourhood of the sea, or in a soil containing rock-salt, a considerably greater quantity of chlorine is, of course, not of hygienic importance. If, however, the normal water of the district contains little chlorine and the well water under examination a considerably greater quantity, this indicates contamination by urine or domestic refuse, which can be confirmed by local inspection. In large towns this is often the case, the ground having become polluted as the result of a dense population over a long period, so that the chlorine content of the water of town wells is often several times greater than that of well water from the surrounding country. The increase of the amount of chlorine is then a measure of the contamination, especially if the residue on evaporation, or the hardness, and also the amount of nitrates is correspondingly larger. In this connection it may be borne in mind that common salt is occasionally added to well water in considerable quantity in order to "improve" it.

7. The amount of sulphuric acid in natural waters is usually small, amounting to some centigrams per litre, but a good water may contain up to 100 mg. per litre. A large quantity of sulphuric acid is only a source of suspicion if not in accordance with the geological conditions of the district.

8. The amount of nitric acid is more important, as it is usually regarded as the final oxidation product of nitrogenous organic matter. A small quantity of nitric acid (10 to 12 mg. per litre) may be admitted, but a larger amount should not be passed, particularly if the normal water of the district contains little nitrate.

9. Ammonia and nitrous acid are either entirely absent, or only present in traces, in really pure drinking water. More considerable quantities of these substances (1 mg. or more per litre) indicate pollution with decaying nitrogenous matter, and therefore point to possible infection. The water of many artesian wells, however, may contain considerable quantities of ammonia and yet be quite admissible as a drinking water or for domestic use, as the presence of ammonia does not then necessarily indicate pollution. From 1 to 5 mg. per litre of ammonia and traces of nitrous acid are normally present in rain water.

In judging a water in which traces of ammonia are found, every care must be taken to guard against contamination of the apparatus and of the liquids used in analysis, which may easily occur through the frequency of traces of this gas in the air of laboratories.

10. Pure spring and well water contains extremely small quantities of organic matter. The oxygen-absorbing power (p. 396) of pure spring water usually amounts to scarcely 1 c.c. of $N/100$ permanganate solution, and that of pure well water to 1 to 2 c.c. per litre; the absorption of several c.c. of permanganate solution, and a considerable oxygen demand (p. 437) are unfavourable indications. When the latter occurs, however, a water can only be rightly excluded for drinking or domestic use if nitrogenous organic matter is also present, as shown by the determination of the albuminoid or proteid nitrogen.

11. The determinations of albuminoid and of proteid nitrogen are to be regarded as the most important chemical methods of examination. Ammonia and nitrous acid are not only present in rain water, but may also be formed by the reducing action of micro-organisms on nitrates; if, however, more than traces of albuminoid or proteid nitrogen are found, decaying or unchanged nitrogenous organic matter is certainly present, and is almost sure to be of animal origin. The determination of albuminoid nitrogen is somewhat lengthy, and only gives reliable results if carried out with care. The determination of proteid nitrogen does not require a distillation and is a useful method for clear waters. With regard to this newer method of investigation the following conclusions may be accepted provisionally:[1]—

i. Pure natural water contains no proteid nitrogen.

ii. The amount of proteid nitrogen may be considered as an index of the amount of nitrogenous organic matter present.

iii. If the proteid nitrogen present amounts to more than 0·1 mg. per litre the water is open to criticism from a hygienic standpoint; 0·2 mg. per litre may be considered as the maximum allowable quantity.

The same limits may be applied to the albuminoid nitrogen.

If the reducing power is considerable, in absence of albuminoid or of proteid nitrogen, this indicates that either organic matter of vegetable origin only is present, or that the decay of organic matter of animal origin has reached its limit: that is to say, that the water has undergone a certain self-purification.

12. Phosphoric acid is only present in pure, natural waters, at most, in traces. The excrements of man and of animals being comparatively rich in phosphoric acid, the presence of more than traces indicates pollution by excreta.

13. Soft, natural waters, which contain both free carbon dioxide and oxygen in solution, take up lead when passed through lead pipes. If lead, even in extremely minute traces, is introduced into the animal organism during a prolonged period, its action is highly injurious; waters containing lead are therefore to be considered directly injurious to health, and should not be allowed for consumption. As, however,

[1] *Cf.* L. W. Winkler, *Z. anal. Chem.*, 1902, 41, 299.

hard water poor in carbon dioxide and oxygen may also dissolve traces of lead under certain circumstances, and as, on the other hand, lead pipes are still largely used for the narrower service pipes on account of their cheapness and convenience, it is often unavoidable to pass traces of lead. The presence of some tenths of a mg. of lead per litre is of serious importance, and water containing 1 mg. of lead or more per litre must be described as poisonous.[1]

14. The bacteriological evidence of pollution or purity has already been briefly referred to (p. 448). Bacteriological standards are subject to modification according to circumstances, but a water may generally be considered of good quality if it contains less than 100 bacteria per c.c. growing on gelatine or agar, and if 50 c.c. do not contain bacteria capable of fermenting glucose or lactose or of clotting milk.

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[1] *Cf.* Houston, *loc. cit.*, *Local Government Board Report*, 1900-1, p. 67; also, Thresh, *loc. cit.*, pp. 86 and 185.

FEED WATER FOR BOILERS

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THE usual impurities found in waters to be used for boiler feed purposes are the bicarbonates and sulphates of calcium and magnesium and the chloride, sulphate and nitrate of sodium. Calcium nitrate and magnesium chloride may also be present and in some cases sodium bicarbonate. When such waters are used for steam raising, the calcium and magnesium salts are deposited, forming scale and sludge, and the sodium salts remain in solution and concentrate in the boiler.

A complete chemical analysis of a boiler feed water therefore necessitates the determination of the dissolved bases and acids in order to ascertain what treatment, if any, is required to render the water suitable for raising steam.

The alkaline earth salts impart what is known as "hardness" to the water; the bicarbonates form the "temporary hardness," or hardness removed on boiling, and the other salts of calcium and magnesium, which cannot be removed by boiling, form the "permanent hardness." The sum of the temporary and permanent hardness gives the "total hardness."

The term temporary hardness is, however, misleading, as calcium carbonate is slightly soluble, and magnesium carbonate distinctly soluble in water, and neither is entirely removed by boiling; the old method of determining the temporary hardness by boiling a known quantity of water for a given time, making up to the original volume with boiled distilled water and testing the hardness by soap solution is thus not accurate, as the hardness remaining after boiling, which is taken to be the permanent hardness, will include some calcium carbonate, and also magnesium carbonate when present in the original water. A better division of the total hardness is "carbonate hardness," due to the bicarbonates of calcium and magnesium, and "permanent hardness," *i.e.* the difference between the total hardness (the hardness due to all the salts of calcium and magnesium) and the hardness due to the bicarbonates of calcium and magnesium.

The actual analysis may be divided into two parts: (i) the volumetric determinations, and (ii) the gravimetric determinations. The volumetric analysis comprises the determination of the "alkalinity" or

bicarbonates, the chlorine, nitric anhydride and the total carbonic acid. The gravimetric work involves the determination of the silica, oxide of iron and alumina, lime, magnesia and sulphuric anhydride.

Volumetric Determinations

1. *Alkalinity.* This is undoubtedly the most important determination since any inaccuracy will affect the calculation of the "probable combinations" (see p. 458). The determination of the alkalinity measures the quantity of the bicarbonates of calcium, magnesium, and (when present) sodium. As it is a titration it is important that an indicator be used which has a sharp end-point, in fact the sensitivity of the indicator is the essential factor. Methyl orange is of no use as the end-point is too indefinite owing to the long transition stage when neutrality is approached, and the *p*H range (2·9 to 4·0) is too far from real neutrality (*p*H 7). The best indicator is diethyl red; the end-point is very sharp and the *p*H range (4·5 to 6·5) much nearer to *p*H 7. The colour changes are yellow (alkaline) to red (acid).

The titration is carried out as follows: To 250 c.c. of the water to be analysed add 4 drops of indicator (1·2 g. per litre in alcohol). The solution should turn yellow if bicarbonates are present; if it turns red the water is acid and the acidity is determined by titration with *N*/10 sodium hydroxide. Run in *N*/10 acid slowly until the colour changes to red; note the quantity of acid used. As a check, add an excess of 2 c.c. of acid, boil for five minutes, allow to cool and titrate back with *N*/10 sodium hydroxide, using phenolphthalein (or, better, *o*-cresolphthalein) as indicator. The direct titration and the back titration should agree. The number of c.c. of *N*/10 acid used, multiplied by 0·88, gives parts per 100,000 of CO_2.

2. *Chlorine.* To 100 c.c. of the water add 3 drops of a 10 per cent. solution of potassium chromate and titrate in the cold with *N*/10 silver nitrate until a permanent reddish colour is obtained after stirring. The number of c.c. of *N*/10 silver nitrate used, multiplied by 3·545, gives parts per 100,000 of Cl. If the water to be titrated contains free alkali, *e.g.* a softened water, or water taken from a boiler fed with softened water, the alkalinity must be exactly neutralised with standard nitric acid before determining the chlorine.

3. *Nitrates.* The quickest method of determining the nitric anhydride is by means of standard indigo solution, made by dissolving indigo in dilute sulphuric acid and standardising, as described below, against a *N*/100 potassium nitrate solution.

To 20 c.c. of the sample placed in a small beaker add 1 drop of N/100 indigo solution, and into this mixture pour quickly 20 c.c. of concentrated sulphuric acid and place on a hot plate for a few minutes. If nitrates are present, the blue colour of the indigo will change to yellow;

if the blue colour is discharged run in standard indigo until a faint blue tint is obtained which persists after standing on the hot plate for five minutes. If, for instance, 5 c.c. of indigo solution has been added, repeat the estimation by taking another 20 c.c. of the water, add 25 c.c. of concentrated sulphuric acid, mix thoroughly by rotating the beaker, and while still rotating run in exactly 5 c.c. of the standard indigo solution; if the blue colour fades very slowly the first estimation may be taken as correct, but if it fades rapidly more indigo solution must be added until the colour persists, and another estimation made using the increased quantity of indigo solution and increasing the strong sulphuric accordingly. The details to be observed are to add to the 20 c.c. of water exactly the same quantity of sulphuric acid as will represent the water plus the indigo solution; to mix quickly and keep hot. The estimation requires experience to get good results, but when once it is understood and one method of working adhered to, the determination of the nitrates by this method is very rapid. If 20 c.c. of the water is used, then each c.c. of indigo solution multiplied by 2·7 gives parts per 100,000 nitric anhydride (N_2O_5). The process rests upon the oxidation of indigo (blue) to isatin (yellow). (*Cf.* p. 475.)

4. *Free Carbonic Acid.* The author recommends Pettenkofer's method, which determines both the free and semi-combined carbonic acid. To carry out the determination 100 c.c. of the water is run into a bottle of about 175 c.c. capacity having a tightly fitting cork; 5 c.c. of a saturated solution of mixed chlorides of barium and ammonium is added (three parts of barium chloride to two parts ammonium chloride) and then 45 c.c. of a standard solution of barium hydroxide (made by dissolving 8 g. of barium hydroxide in 1 litre of boiled, distilled water, filtering and determining the exact strength by titration with $N/10$ nitric acid, using lacmoid as indicator). Cork the bottle, shake well and allow to stand until the precipitate has settled. Fifty c.c. of the clear solution is withdrawn by means of a pipette, run slowly into a beaker, 2 or 3 drops of lacmoid added and the solution titrated with $N/10$ nitric acid. The number of c.c. of acid required, multiplied by 3, and the result subtracted from the amount of acid required to neutralise 45 c.c. of the standard barium hydrate solution, multiplied by 2·2, gives the total free and semi-combined carbonic acid. If the amount of semi-combined carbonic acid, found by the determination of alkalinity, be subtracted the result will be the free carbonic acid in parts per 100,000.

Gravimetric Determinations

This portion of the analysis involves the determination of the silica, oxides of iron and alumina, lime, magnesia and sulphuric anhydride.

1. *Silica.* To 250 c.c. of the sample add a few drops of concentrated hydrochloric acid, evaporate to dryness, ignite the residue, gently moisten with concentrated hydrochloric acid, add 20 to 25 c.c. of distilled water and digest on a hot plate until all the soluble portion of the residue is dissolved. Filter through an ashless paper, wash until free from acid, dry, ignite in a platinum crucible and weigh. The gain in weight multiplied by 400 gives parts per 100,000 of silica (SiO_2).

2. *Iron and Alumina.* To the filtrate add about 10 c.c. of a saturated solution of ammonium chloride (to keep the magnesium in solution) and a few drops of nitric acid, followed by just sufficient ammonium hydroxide to leave a distinct smell of ammonia; the solution is then boiled, filtered through an ashless paper, the paper well washed and dried, ignited in a porcelain crucible and weighed. The gain in weight, multiplied by 400, gives parts per 100,000 of the oxides of iron and aluminium (Fe_2O_3 and Al_2O_3). Unless there is much iron or alumina present it is rarely necessary to separate the mixed oxides.

3. *Calcium.* To the filtrate from the determination of the oxides sufficient ammonia is added to render the solution strongly alkaline, and then an excess of ammonium oxalate. The precipitated calcium oxalate is digested on a hot plate until it settles, filtered through an ashless paper, the paper well washed with distilled water, dried and ignited in a platinum crucible over a high temperature burner to constant weight. The increase in weight multiplied by 400 gives parts per 100,000 of lime (CaO). The filtrate should be tested with ammonium oxalate to ensure that all the calcium has been precipitated. If preferred the lime may be determined by washing the precipitate with dilute ammonia into a beaker, adding sulphuric acid and titrating with standard potassium permanganate.

4. *Magnesium.* The filtrate from the calcium determination is made strongly alkaline by the addition of half its volume of 0·88 ammonia and 10 c.c. of sodium phosphate solution is added. The beaker should be covered with a clock glass and allowed to stand for several hours, preferably overnight, to allow the crystalline precipitate of ammonium magnesium phosphate to settle out. The precipitate is then filtered, washed with dilute ammonia (1 : 2), the paper dried slightly and ignited in a porcelain crucible very slowly at first, and the temperature gradually raised until the contents of the crucible are practically white. The increase in weight multiplied by 144 gives parts per 100,000 of magnesia (MgO).

5. *Sulphuric Anhydride.*—The determination of the sulphuric anhydride is most conveniently carried out on a separate portion of the sample. For this purpose 250 c.c. is evaporated to a small bulk with the addition of a few drops of concentrated hydrochloric acid,

10 c.c. of barium chloride added to the hot solution, and the whole allowed to digest on a hot plate until the barium sulphate settles out, and the supernatant liquid is clear. After filtering through an ashless paper the precipitate is washed with distilled water until free from chlorides, the paper dried, ignited in a porcelain crucible at a gentle heat, allowed to cool and weighed. The gain in weight multiplied by 137 gives parts per 100,000 of sulphuric anhydride (SO_3).

Calculation of the "Probable Combinations"

This is made by calculating the CO_2 as found under "Alkalinity" to calcium carbonate; if there is more than sufficient calcium to combine with all the CO_2 the balance is first calculated to calcium sulphate and any remaining to calcium nitrate or calcium chloride. If the CO_2 is in excess of the lime, the balance is first calculated to magnesium carbonate and any excess to sodium carbonate. The balance of the magnesia, or the total if no magnesium carbonate is present, is first calculated to magnesium sulphate, and if in excess of the sulphuric acid the remaining magnesia is calculated to magnesium chloride. If the sulphuric acid is in excess of that required to combine with all the magnesia, the balance is calculated to sodium sulphate. The nitric anhydride is calculated to sodium nitrate and the chlorine to sodium chloride.

This method gives the most probable composition of the water from a boiler feed point of view.

Calculation of the Amounts of Lime and of Sodium Carbonate required for the Treatment of Feed Water

Practically all waters require treatment in order to render them fit for boiler-feed purposes. An ideal feed water should be as soft as possible and very slightly alkaline to phenolphthalein, as in this condition it will not deposit a hard scale, neither will it be corrosive. To remove the carbonate hardness, lime is required and the amount can be determined by calculating how much is necessary to combine with the total CO_2 by multiplying the CO_2 found by 0·127; this will give pounds of lime (CaO) per 1000 gallons of water to be treated. In addition, lime will be required to remove the magnesia. The amount is found by multiplying the content of magnesia by 0·14; the addition of these two quantities will be the total lime required per 1000 gallons of water.

If the water also contains permanent hardness, sodium carbonate will be needed in addition to lime. The amount is determined by calculating the quantity required to combine with the calcium and magnesium salts present in the sample other than calcium and

magnesium carbonates and adding the amounts so found together. As commercial lime is never 100 per cent. pure, it is advisable to increase the amount of lime calculated by 10 per cent. and the sodium carbonate also by an equivalent amount.

Testing Treated Water

Hardness. A properly treated water should have a low degree of hardness (say 2°) and a low alkalinity. The best method of determining the hardness is by means of soap solution made to what is known as "Wanklyn's Standard" (1 c.c. of soap = 1° hardness = 1 grain of calcium carbonate per gallon). To carry out the determination 70 c.c. of the water is measured into a stoppered bottle and the soap solution added from a burette, a few drops at a time, and shaken thoroughly after each addition until a lather is obtained which remains permanent after standing for five minutes. The total number of c.c. of soap used minus one (the quantity required to give a lather with distilled water) gives the total hardness of the water in English degrees (grains per gallon).

Alkalinity. This is determined by taking 70 c.c. of the water and adding 4 drops of *o*-cresolphthalein (or phenolphthalein); the water should turn pink. Titrate with $N/50$ acid until the colour is discharged, add 4 drops of diethyl red and complete the titration. If the cresolphthalein figure is more than half the total, both alkali hydroxide and carbonate are present. If the cresolphthalein figure is exactly half the total, the alkalinity is all carbonate; if the cresolphthalein figure is equal to the total, the alkalinity is all hydroxide. If the total hardness found by the soap test is high (say over 4°) and the alkalinity to cresolphthalein is high, too much lime has been used in the softening process; if the hardness is high and the alkalinity to cresolphthalein low or absent, too little of both lime and sodium carbonate have been used; if the hardness is very low and the alkalinity high, too much lime and sodium carbonate have been used. When properly treated a feed-water should have an alkalinity of 2-3 to cresolphthalein, and 3-4 to diethyl red.

Oil. This is very detrimental in boiler feed waters as it causes priming; furthermore, a very thin film of oil results in the boiler tubes becoming overheated and bulged. The amount of oil can be determined as follows:—Place 250 c.c. of the suspected water in a stoppered separating funnel, add 1 c.c. of hydrochloric acid (conc.), shake well and add 25 c.c. of ether. Mix thoroughly, and allow to stand until the liquid has separated into two layers. The aqueous layer should now be perfectly clear; if it is not, add more ether and shake again. If oil is present in any appreciable quantity, the ether will be found to have a

yellow tinge; very small amounts of oil may not colour the ether. After separating the water run the ether extract into a very small tared beaker and evaporate off the ether either on an electric hot plate or by placing the beaker in hot water. If the latter method is used, thoroughly dry the outside of the beaker after all the ether has evaporated, allow to stand in the balance case until cold and weigh. The gain in weight multiplied by 400 gives parts per 100,000 of oil.

Note.—If it is desired to express the results of the analysis in grains per gallon, instead of parts per 100,000, the figures given above should be multiplied by 0·7.

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SEWAGE AND EFFLUENTS

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OWING to the very varied character of effluents, and especially of those from the heavy and fine chemical industries, it is almost impossible to present a concise summary of the methods required for their analytical examination.

Effluents may be divided into those containing mainly mineral constituents and those consisting chiefly of nitrogenous organic substances. The examination of the former is essentially the same as that of drinking water, with a special regard to such abnormal constituents as are due to the particular industry concerned. Effluents containing mainly nitrogenous organic matter necessitate quite different methods of examination, which will be more specifically described in this section.

The constituents that may occur in the different kinds of effluents are summarised in the following list; owing to the great number of types of effluents, the list is in no way to be regarded as complete.[1, 2]

I. Effluents containing mainly Mineral Constituents from:—

1. *Coal mines:* Sodium, barium, calcium, strontium, and magnesium chlorides, ferrous and ferric sulphates, and free sulphuric acid.

2. *Strontianite mines;* Strontium, calcium, and magnesium carbonates or sulphates.

3. *Salt works and brine springs:* Sodium, calcium, strontium, and magnesium chlorides.

4. *Potassium chloride works, salt refineries, and bleach works:* Calcium and magnesium chlorides and, from bleach works, manganous chloride also.

5. *Pyrites mines, pyrites dressing works, and waste-heaps at coal mines:* Free sulphuric acid, ferrous sulphate, and sometimes zinc sulphate.

[1] *Cf.* J. König, *Die Verunreinigung der Gewässer, deren schädliche Folgen nebst Mitteln zur Reinigung der Schmutzwässer*, 2nd edition, 1899.

[2] *Cf.* Fowler and Ardern, *Disposal and Purification of Trade Effluents*, 7th Int. Cong. App. Chem., London, 1909.

6. *Zinc blende mines, galena mines, and zinc blend stamping mills:* Zinc sulphate and bicarbonate.

7. *Wire works:* Free sulphuric acid and ferrous and ferric sulphates, or free hydrochloric acid and the corresponding chlorides, according to the cleaning liquor used.

8. *Galvanising works:* Free hydrochloric acid and ferrous chloride.

9. *Brass foundries and silver etching works:* Free sulphuric acid and copper sulphate.

10. *Pyrites residues:* Iron, zinc, or copper sulphates, and free sulphuric acid, according to the material used.

11. *Alkali works:* Calcium and sodium sulphides and polysulphides, calcium chloride, and calcium hydroxide.

12. *Slag waste-heaps:* Calcium and sodium sulphides.

13. *Bleaching works:* Calcium chloride and hypochlorite.

14. *Gas works and coke ovens:* Calcium and ammonium sulphides and thiocyanates, phenols, and tarry products.

15. *Potassium ferrocyanide works:* Sulphur and cyanogen compounds.

16. *Colour works and dye works:* Oxides of zinc, tin, lead, copper, and chromium, antimony, arsenic, dyes, and mordants.

17. *Electroplating works:* Potassium cyanide and free acids.

18. *Tanneries:* Lime, sodium sulphide, and thiosulphate, chromium salts, free acids.

II. Effluents containing mainly Nitrogenous Organic Matter

These include the sewage of towns, and the effluents from slaughter-houses, sugar and starch factories, breweries, distilleries, dairies, paper mills, wool-combing works, cloth factories, glue factories, tanneries, etc.

Usually, in England, sewage and manufacturing effluents are treated together at the sewage purification works, and many of the analytical methods to be described are applied to the control of the method of purification adopted, more especially when the so-called "biological" or bacterial treatment of sewage is employed.

In the examination of all these effluents special attention must be directed to the amounts of suspended and dissolved organic matter, the amount of oxygen needed for their oxidation, and the amount of nitrogen in its various forms. In effluents from breweries and distilleries attention must also be paid to the presence of yeast cells, dextrin, starch and sugars; the two latter constituents must also be considered in effluents from starch factories. The effluents from wool-combing works and from cloth factories must be tested for fats, soaps, and arsenic; effluents from tanneries for arsenic, and for sodium and calcium sulphides.

The variety in the composition of effluents is evident from this

summary. It is to be borne in mind that the composition of the effluents from any one works is not always the same, but may vary frequently even during a short period of time. It is therefore of the very greatest importance, for a correct examination of an effluent water, that the samples should be taken with care and judgment; incorrect sampling is more often the cause of an erroneous conclusion than the actual analytical examination.

SAMPLING[1]

The vessels and corks used for taking the sample must of course be clean, and both should be thoroughly rinsed with the sample before filling. The sampling apparatus devised by F. C. G. Müller[2] is simple, convenient, and reliable, and permits of the sample being collected from any depth. It consists of a stirrup B (Fig. 81) soldered to a lead plate A, weighing 2 kilos. and suspended by means of the spiral spring E and the hook F, to a sounding-line. A bottle, D, of about 400 c.c. capacity, is fastened to the stirrup by means of the clamp C, and is fitted with a double-bored rubber stopper, both holes of which are closed by the U-shaped stopper H; the latter is attached to the chain J, which passes through the spiral to F, and is not quite taut.

To take a sample, the apparatus is lowered into the water and the line smartly jerked, when the stopper H will be removed, as the spiral spring elongates more quickly than the heavy mass below can follow; the water then enters through the small tube G placed in the one opening, whilst the air escapes through the other. After eighty seconds, at most, the bottle is filled and can be taken up.

F
E
J H
C C
B B
G D
A
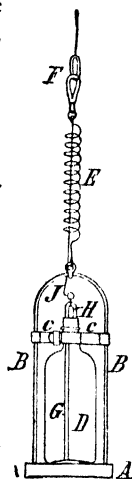
FIG. 81.

From 2 to 4 litres of the water must always be collected for examination.

If a report on the water is to be made for a court of law or for an administrative authority, it is imperative that the samples should be collected by the responsible expert.

The most essential point in sampling an effluent water is that the sample should really represent a good average of the effluent. It is therefore necessary to determine whether the effluent flows continuously, and is of constant composition, or whether the composition alters during the course of a day, or whether the effluent only flows periodically and not continuously during the whole day. In the first case, when the effluent flows continuously and is of uniform composition, it is

[1] A full account of the various forms of sampling apparatus is given by Schumacher, *Gesundheitz-Ingenieur*, 1904, pp. 418, 434, and 454.

[2] *Forschungsber. a. d. biolog. Station zu Plön*, 1903, 10, 189.

unimportant at what hour the sample is taken. If the composition alters during the day, it is advisable to take samples at short intervals, of about ten to fifteen minutes, and to collect these together in a clean tub which has been previously well rinsed out with the effluent. The contents of the tub are then thoroughly mixed and a sample of the whole taken for analysis; or samples may be taken every ten to fifteen minutes, over periods of about two hours, at intervals during the day, and the whole mixed to obtain a final sample. For exact work, these samples should be mixed in proportion to the rate of flow at the time each was taken. This must be ascertained by a continuous gauging during the period of sampling.

If the effluent is discharged intermittently, the sample must be taken during the time that it is being run off; if the composition varies, a sample is taken each time the water is run off, and a mixture made of the samples thus obtained in the proportion of the actual quantities of water which they represent.

If the object of the examination is to test the efficiency of a method of purification, care must be taken that the purified water corresponds to the unpurified effluent. To satisfy this condition it is necessary to find out how long the effluent takes to flow through the purifying plant, and this time must be allowed to elapse between the collection of the samples of unpurified and purified water; the two samples must, of course, be collected in exactly the same manner.

When an effluent flows into a river, the question that has usually to be considered is whether the effluent has imparted such properties to the river water as are likely to be injurious to any of its specific uses. The mere detection of harmful constituents in the water is insufficient. Samples must be collected both above and below the point of entry of the effluent, and care taken that the sample collected above the point of entry has not mixed with the effluent through back-wash; it is also important to consider whether the water above the inflow of the effluent may have been previously contaminated by other effluents. The sample taken below the entry of the effluent must be collected at a point where the effluent has had time to mix thoroughly with the river water. This mixing is promoted by curves in the river, dams, bushes, etc. In the case of an even river with a slow current, effective mixing may only have been attained some miles below the point of entry of the effluent. In collecting the sample below the point of entry, it is also necessary to observe whether other feeders have supplied the river between the entry of the effluent and the place selected for taking the sample; should this be the case, a sample of each feeder must be collected and examined.

Samples should be taken from each bank and from the middle of the stream, also from the surface and from various depths, and the examina-

tion of the water made on a mixture of the samples collected in this manner; this method of taking samples from various parts is especially necessary in examining the water of stagnant pools, ponds, and lakes.

In tidal rivers, the state of the tide must be noted and samples taken accordingly; pollution may, of course, be carried up the river on a rising tide.

In some cases, especially where many rapidly varying effluents flow into a stream, the extent of the influence or pollution of each effluent can be found by examining the composition of the water and determining, in addition, the quantity of flow of the stream and of each effluent; the degree of pollution introduced at high-, low-, and mid-water can then be calculated. The determination of the quantities of water is best dealt with by a hydraulic engineer.

Light may in some instances be thrown on the cause of pollution by an examination of the mud, or of the deposits on stones and plants, or by the presence of damaged plants and trees, or of dead fish. The fauna and flora of the water should be noted when collecting the sample.

CHEMICAL EXAMINATION

A. Preliminary Examination on the Spot

In the preliminary examination the following points are dealt with:—

1. *Appearance of the Water.* Whether clear, turbid, coloured, etc. The extent to which a turbid or coloured water is harmful can only be determined by the examination of the suspended matter causing the turbidity; the turbid appearance of a water is not in itself decisive as to whether it is harmful or not.

2. *Smell.* Whether due to hydrogen sulphide, sulphur dioxide, free chlorine, ammonia, turnips, beet, yeast-water, etc.

3. *Reaction.* This is determined by holding litmus paper in the running water.

4. *Temperature.* A sensitive thermometer is held in the flowing water until it indicates a constant temperature; readings must be taken in various positions and at various depths. In sampling from manholes or other places where the actual liquid is not readily accessible, it is convenient to attach the thermometer to a small receptacle which can be lowered, along with the thermometer, into the liquid; the temperature can then be read without appreciable error, on bringing the receptacle to the surface.

5. *Nitrous Acid.* A qualitative test with potassium iodide, starch solution and dilute acetic acid, or with meta-phenylenediamine, is sufficient.

6. *Free Gases and Volatile Acids.* If oxygen, carbon dioxide, hydrogen sulphide, chlorine, hydrochloric acid, etc., are to be quantitatively determined, this must either be done on the spot, or they must be fixed in such a way that they do not alter during transit. Oxygen can be absorbed either by L. W. Winkler's method (p. 433), carbon dioxide by addition of lime water free from carbon dioxide, hydrogen sulphide by addition of cadmium chloride, or of sodium arsenite and alkali, hydrochloric acid by silver nitrate solution, etc., and the solutions obtained further examined in the laboratory as described below.

7. The *Bacteriological examination* must be started on the spot, preferably in Petri dishes, and continued in the laboratory.

B. Examination in the Laboratory

The examination in the laboratory must always be made as soon as possible after the collection of the sample, especially if the effluent contains much organic matter; the latter readily decomposes on keeping, being partially converted into gaseous products, and partly causing solution of suspended organic matter, or the precipitation of organic substances from solution. If it is impossible to examine the sample at once, this must be taken into account in interpreting the results, or a preserving agent such as dilute sulphuric acid or chloroform must be added when the sample is collected. The former is used as an addition to filtered effluent waters in which the oxidisability, the organic nitrogenous compounds, ammonia, and organic carbon, are to be determined, and the latter as an addition to unfiltered water in which the residue on evaporation, the suspended matter, loss on ignition, nitric and nitrous acids, and chlorine are to be estimated. Whenever, possible, however, it is preferable to pack the samples in an ice-box till they can be examined.

The above preliminary tests must be, as far as possible, controlled and repeated in the laboratory. The smell is often only noticeable after warming to 40° to 50°, or on rinsing round a small sample in a beaker.

When, in disputed cases, the water is examined by several chemists, uniform methods of analysis should be employed. The methods given below have so far been found to be trustworthy.

1. Residue on Evaporation and Loss on Ignition

Two hundred c.c. of the water is evaporated to dryness in a previously ignited and weighed platinum dish; the residue is dried in an oven at 105° to 110° for one hour, weighed after allowing to cool in a desiccator, and the drying repeated until the weight is constant.

The residue is then heated to redness in the platinum dish, moistened with ammonium carbonate and again gently ignited. The difference between the weight of the residue on evaporation and that obtained on ignition gives, fairly accurately, after allowing for water of crystallisation, the amount of organic matter in the water; the residue on ignition represents the anhydrous mineral matter.

2. Suspended and Dissolved Organic and Inorganic Matter

From 200 to 1000 c.c. of the water, according to the amount of suspended matter present, is filtered through a filter paper previously washed, dried at 100° to 105°, and weighed. The residue on the filter is washed twice with distilled water, dried at 100° to 105°, and weighed, then ignited, and again weighed. The total residue represents the amount of suspended organic and inorganic matter, the ash, after deduction of the filter ash, the amount of inorganic matter, and the difference, the amount of organic matter.

To identify the inorganic constituents the ash is dissolved in hydrochloric or nitric acid, and the solution examined in the usual manner.

The dissolved inorganic and organic matter is determined in the filtrate and washings, from the above residue, or in an aliquot part, as described under 1 (p. 466).

If the water does not filter well, so that a change might occur during filtration, it is advisable to filter a well-mixed portion of the sample through a dry, pleated filter-paper, and to determine the residue on evaporation and on ignition in 200 c.c. of the filtrate, and also in 200 c.c. of the original unfiltered water. The difference between the losses on ignition from the unfiltered and filtered water gives the amount of suspended organic matter, the difference between the residues on ignition, the amount of suspended mineral matter. The dissolved organic and inorganic matter are found from the loss on ignition and the weight of the residue from the filtered water.

If the water contains free lime, carbon dioxide is first passed through in excess, and the determinations then made as above; the carbon dioxide corresponding to the free lime is deducted from the total residue.

When the sample contains a large amount of suspended matter, *e.g.* storm water, a sufficiently accurate determination may be made by allowing, say, 500 c.c. of the sample to stand, when the greater part of the suspended matter settles out.[1] The fairly clear liquid is then syphoned off, and the deposit washed on to a smooth, toughened filter-paper (*e.g.* Schleicher and Schüll, No. 575), washed, and dried in the air-bath at 100° to 110°. After drying, the suspended matter can

[1] Fowler, *Sewage Works Analyses*, p. 106.

be scraped off the smooth paper into a weighed crucible and weighed. On igniting, moistening with ammonium carbonate, and reheating the proportion of mineral matter is obtained as before.

Where a large number of determinations have to be made, they may be much facilitated by the use of a centrifugal machine. There are many types of these, all depending on the fact that if a solution containing suspended particles is rapidly whirled round, the particles tend to collect at the bottom of the liquid if they are heavier than the latter, and at the top if they are lighter. The separated particles can readily be washed by decantation, transferred to a crucible, dried, and weighed.

3. The Determination of Colloidal Matter[1]

The organic and other matter in sewage and effluents is partly present in the colloidal state. The better the effluent the greater is the proportion of the total matter present in true solution, and the less the difference in composition before and after passage through a parchment membrane.

The colloidal matter should be estimated after removal of the grosser suspended matter by settlement for a sufficient period.

The best method for dialysis is to employ "sausage skin" parchment paper dialysers filled with water and immersed in the solution to be dialysed, contained in long glass cylinders. The solution is left to dialyse until the chlorine content of the solution is found to be the same on both sides of the dialyser. A determination of the "oxidisability" or of the albuminoid nitrogen, within and without the dialysers, will then give a measure of the ratio between the colloids and crystalloids thus:—

If x = value obtained for the solution outside the dialyser,
y = value obtained for the solution inside the dialyser,
d = ratio of total volume of solution to volume inside the dialyser (or ratio of original to final chlorine content).

$$\text{Ratio: } \frac{\text{colloids}}{\text{crystalloids}} = \frac{x-y}{dy}$$

Similar information is more rapidly obtained when the liquid is clarified by boiling with sodium acetate and ferric chloride, filtered through paper, and the original liquid and the filtrate analysed.

In this case, 200 c.c. of the sample is treated with 2 c.c. of a 5 per cent. solution of ferric chloride, and 2 c.c. of a 5 per cent. solution of sodium acetate, the mixture boiled for two minutes, filtered, cooled, and

[1] *Cf.* Kröhuke and Biltz, *Hygienische Rundschau*, May 1904; Fowler and Ardern, *J. Soc. Chem. Ind.*, 1905, **24**, 483; Fowler, Evans, and Oddie, *ibid.*, 1908, **27**, 205; J. H. Johnston, *J. Royal Sanitary Inst.*, 1906; Rolants, *7th Int. Cong. App. Chem.*, London, 1909, Section viii*a*, 161-169.

the oxidisability or the albuminoid nitrogen determined in both the unclarified and the clarified sample.

Then, if x = value obtained for the unclarified sample,
y = value obtained for the clarified sample.

$$\text{Ratio}: \frac{\text{colloids}}{\text{crystalloids}} = \frac{x-y}{y}$$

Aluminium acetate may be used in the above method instead of ferric acetate. Rolants has used powdered talc with the idea of avoiding precipitation of organic matter from crystalloidal solution.

4. Oxidisability or Oxygen-consuming Power— "Oxygen Absorption"

The quantity of potassium permanganate used up by a sample of water does not give an absolute measure of the amount of organic matter in a water, as the oxidisability of the organic substances varies greatly and is seldom complete under the conditions prescribed for the determination. Comparable values may, however, be obtained for liquids of the same or similar origin.

The most satisfactory results are obtained by making the determination on the filtered sample of the liquid. In comparative tests on purified and unpurified liquids, it is advisable to choose such dilutions that approximately equal quantities of permanganate are used for equal volumes of the diluted samples. Excess of permanganate should always be present. To ensure this, the dilution should be such that the liquid remains red on boiling with 20 c.c. of $N/100$ permanganate solution.

The details for the estimation are given under Drinking Water, p. 397. As it is often necessary, in determining the oxygen absorbing power of effluents, to dilute the sample with distilled water, attention should be paid to the fact that distilled water is seldom free from organic matter. H. Noll[1] has accordingly proposed to titrate the distilled water used with the permanganate solution, and then immediately to run 15 c.c. of $N/100$ oxalic acid solution into the titrated liquid, and determine how much permanganate solution this requires; the difference between the two results gives the oxidisability of the distilled water, which is used as a correction in the determination. Or, a drop or two of permanganate solution may first be added to the water used for dilution or for making up the standard permanganate solution, till a very faint permanent pink tinge is obtained.

From the quantity of potassium permanganate solution required to oxidise the organic matter, the amount of the latter in the water may be expressed in various ways. Supposing that 10 c.c. of permanganate

[1] *Z. angew. Chem.*, 1903, **16**, 748.

solution corresponds exactly to 10 c.c. of oxalic acid solution, and that 10 c.c. of the former is originally added and 5 c.c. titrated back, then the 100 c.c. of water examined contains organic matter which requires 5 c.c. of permanganate solution, per litre, for its oxidation, or 15·8 mg. permanganate or 4·0 mg. oxygen per litre.

The following methods of determining the oxygen-consuming power or oxygen absorption are also used.[1]

Four Hours' Test. Fifty c.c. of the liquid, or other volume, according to the oxygen absorbing power, is treated with 10 c.c. of sulphuric acid (1 : 3) and 50 c.c. of potassium permanganate solution (10 c.c. = 1 mg. oxygen); the mixture is allowed to stand in a closed bottle for four hours, and is shaken from time to time if suspended matter is present. If the colour is noticeably weaker before the end of the four hours, more acid and permanganate are added. After four hours a few drops of 10 per cent. potassium iodide solution are added and the amount of liberated iodine determined by titration with sodium thiosulphate solution (1 c.c. = 2 c.c. permanganate solution); from this the amount of unused permanganate, and hence of absorbed oxygen, is calculated.

Tidy's Method[2] is similar to the preceding. The permanganate solution is allowed to act for two or three hours on the acidified water, and the undecomposed permanganate determined according to the method given under the four hours' test.

In other cases the duration of the action of the permanganate is limited to three minutes ; this is called the *Three Minutes' Test.*

Incubator Test. The amount of oxygen taken up from the permanganate in the three minutes' test is first determined. A bottle is then completely filled with the sample, and kept closed, in an incubator, for six or seven days[3] at 27°. The amount of oxygen absorbed in three minutes is then again determined. If putrefaction has taken place, the amount of oxygen absorbed in three minutes will have increased, in consequence of the greater oxidisability of the products of decomposition ; if, on the other hand, the sample has remained fresh, no increase but possibly a slight decrease will have occurred, due, in the latter case, to slight oxidation of the impurities at the expense of nitrates or of air dissolved in the water.

5. Alkalinity

The alkalinity of a water may be caused by free calcium hydroxide, ammonia, etc. It is determined by titration with $N/10$ or $N/5$ hydrochloric acid, using methyl orange as indicator, and is expressed in

[1] *Cf.* Fowler, *Sewage Works Analyses*, pp. 21-37. [2] *J. Chem. Soc.*, 1879, 35, 66.

[3] Two days at 37° is preferred by the Committee of the Assoc. of Managers of Sewage Disposal Works (see Ministry of Health pamphlet on *Methods of Analysis*, p. 31).

terms of mg. of CaO per litre, or in mg. per litre of the principal base present. (*Cf.* pp. 389 and 455.)

6. Free Acids

If alkalis or alkaline earths are the only bases present, the free acids may be determined by titration with *N*/10 sodium hydroxide solution, using litmus as indicator. If other metals (iron, zinc, copper) are also present, the total amounts of acids and of bases must be determined and calculated to salts; if there is an excess of total acids, that acid which, according to the nature of the effluent, may be supposed to be present in excess, is assumed to be free.

7. Nitrogen

The quantity of total nitrogen and that of the individual nitrogen compounds is of special importance in forming a judgment on the character of an effluent.

A. Total Nitrogen. The Kjeldahl-Jodlbaur Method. Two hundred and fifty to five hundred c.c. of liquid is boiled down with 25 c.c. of phenol-sulphonic acid (200 g. phosphoric anhydride and 40 g. phenol in 1 litre of concentrated sulphuric acid) in a round-bottomed Jena glass flask of about 700 c.c. capacity, over a naked flame; after cooling, 2 to 3 g. of zinc dust free from nitrogen and 1 g. of mercury are added, the whole allowed to stand for a short time, and then heated until the liquid is colourless. The residue is then treated as usual and the liberated ammonia absorbed by sulphuric acid. Full details of the method are given in the section on Fertilisers, p. 496 *et seq.*

The following process, based on the Ulsch modification of the Kjeldahl method, has been found satisfactory for determining the total nitrogen in sewage and effluents. (Fowler.)

Fifty c.c. or more of the sample is taken and the free ammonia distilled off with steam after the addition of a little sodium carbonate. The liquid is then transferred to a 300 c.c. round-bottomed Jena flask, 2·5 g. of zinc dust and 1 drop of platinic chloride solution added, the volume made up to 150 c.c. with ammonia-free distilled water (carefully washing any adherent particles in the neck into the flask), and 10 c.c. of a 20 per cent. sulphuric acid solution added to the mixture. Care must be taken on the addition of the acid to prevent frothing over, by gently swirling the flask round, or by tilting it into an almost horizontal position, until most of the effervescence has subsided. The flask is then placed on a sand-bath in an inclined position and gently heated until the bulk is reduced to about 50 c.c.; after cooling, 0·1 g. of pure copper oxide is added and well mixed with the residue, and then

20 c.c. of concentrated sulphuric acid drop by drop, the same means being adopted as before to prevent frothing over; when the greater part of the effervescence has subsided, four more drops of platinic chloride are added, care again being taken to obviate frothing. The contents of the flask are then heated carefully over a small, free flame about 1 inch high, so that the flame does not reach the edge of the surface of the liquid; the heating is continued until the liquid is completely charred and has a pale green or greenish-grey colour. The contents of the flask are cooled, diluted carefully with ammonia-free distilled water, the crystalline residue dissolved, the solution again cooled, transferred to a 300 c.c. flask, and made up to the mark with the ammonia-free distilled water.

One hundred and fifty c.c. of this solution is placed in a round-bottomed flask fitted with a tap-funnel and attached to a condenser, the receiver of which dips into an Erlenmeyer flask containing 20 c.c. of *N*/10 sulphuric acid solution; 2 or 3 drops of phenolphthalein are added to the solution, strong potassium hydroxide solution run in till alkaline, and the mixture distilled with steam until 200 c.c. have passed over into the sulphuric acid. A further 50 c.c. may be distilled over and tested for ammonia by Nessler's reagent. The excess of acid is titrated back with *N*/20 potassium hydroxide, using methyl orange as indicator, and the result calculated in terms of nitrogen. A blank experiment should always be made with the reagents used.

If nitrates are present, the ammonia produced by their reduction, as determined in a separate experiment, must be deducted from the total amount found. It is safer, in this case, to determine the "nitrate" nitrogen by starting two determinations as described, and determining the ammonia produced in the first stage of the process by stopping it at the end of the boiling down with dilute sulphuric acid and zinc dust, making alkaline, distilling with steam, and titrating or Nesslerising the distillate.

By subtracting the "albuminoid" nitrogen, as determined by distillation with alkaline permanganate, from the total "organic" nitrogen, the amount of what may be termed "residual" nitrogen is obtained.

In the case of dry, solid matters such as sludge, 0·5 g. is taken for analysis, and the preliminary distillation of the free ammonia omitted.

J. Campbell Brown[1] recommends evaporating and subsequently igniting the sample in a glass or copper retort with a mixture of potassium hydroxide and potassium permanganate, the liberated ammonia being estimated by Nessler's solution; he states that this method is as precise as the Kjeldahl process and less troublesome to carry out.

[1] *J. Chem. Soc.*, 1905, 87, 1051.

B. Ammoniacal Nitrogen. (*Cf.* p. 413.) Ammonia is tested for qualitatively by adding 0·5 c.c. of sodium hydroxide solution and 1 c.c. of sodium carbonate solution to about 100 c.c. of the liquid, allowing to settle, and testing the clear solution with Nessler's reagent; a pale yellow to reddish brown coloration or precipitate is formed, according to the amount of ammonia present.

For the quantitative determination, a definite volume of the liquid is distilled with ignited sodium carbonate, and the liberated ammonia either absorbed in titrated sulphuric acid or estimated colorimetrically. Ignited magnesia is sometimes used, but it is regarded by some writers as likely to cause a decomposition of nitrogenous organic substances, and thus lead to high results.

The colorimetric method is only suitable for waters which do not contain a large proportion of ammonia; otherwise the sample must be largely diluted and the experimental error is then correspondingly increased. The preparation of solutions containing known amounts of ammonia for the colorimetric comparison can be avoided by using a colorimeter wlth a permanent colour scale such as that devised by J. König.[1]

A large number of comparative determinations can, however, be readily carried out by means of the Stokes colorimeter. This instrument consists essentially of two glass cylinders, each of 100 c.c. capacity, joined at the base by a rubber tube. One of the cylinders is graduated into c.c., and can slide in a clamp which is attached to a vertical brass support; the second cylinder is plain and rests on a sloping glass plate, beneath which a piece of white opal glass is placed. One hundred c.c. of ammonia solution of known strength, together with 4 c.c. of Nessler's reagent, are placed in these cylinders as the standard for comparison.

The sample to be tested is similarly treated with Nessler's reagent and placed in a third cylinder of corresponding dimensions. The graduated cylinder of the instrument is then moved up and down until the tints in the plain cylinder and in the third cylinder, containing the sample, correspond. This identity of tint is best judged by observing the cylinders through a card perforated with two holes about half an inch in diameter, coinciding with each cylinder. From the reading on the graduated cylinder the amount of ammonia can then be calculated.[2]

C. Nitrous Nitrogen. (*Cf.* p. 407.) To test qualitatively for nitrous acid, either a clear sample is used, or one which has been clarified by adding 3 c.c. of sodium carbonate solution (1 : 3), 0·5 c.c. of sodium hydroxide solution (1 : 2), and a few drops of alum solution (1 : 10). About 50 c.c. of the sample is well mixed with 0·5 c.c. of zinc iodide-starch solution and 5 to 6 drops of dilute sulphuric acid.

[1] *Chem. Zeit.*, 1897, **21**, 599.
[2] *Cf.* Fowler, *Sewage Works Analyses*, pp. 50-52.

The starch solution is prepared by dissolving 20 g. of zinc chloride in 100 c.c. of water, filtering, and adding to the boiling filtrate 4 g. of starch mixed into a thin paste with a few c.c. of cold water, with constant stirring. The whole is diluted to 1 litre, the flocculent material allowed to settle, and the solution filtered through a small jelly-bag.[1] Equal volumes of this solution and of potassium iodide solution are mixed for use.

A blue coloration is formed, which appears either at once or only after some minutes, according to the quantity of nitrous acid present; if the coloration appears only after about five minutes, it may be due to organic matter or to ferric salts. The error caused by the presence of ferric salts may be avoided by the use of a sulphuric acid solution of meta-phenylenediamine instead of the zinc iodide-starch solution. The test is then made by adding 1 to 2 c.c. of dilute sulphuric acid and 1 c.c. of the diamine solution to 100 c.c. of the water, in a tall glass cylinder. According to the amount of nitrous acid present, a brown or yellowish-brown to reddish coloration, due to the formation of an azo-dyestuff, is obtained.

The quantitative determination of nitrous acid is best effected colorimetrically. An accurate colorimetric method is that of G. Lunge and Lwoff (*cf.* p. 408). König's colorimeter has also been adapted for this estimation, and is very serviceable for the purpose. To carry out the determination, 100 c.c. of the clear or clarified sample is placed in a Hehner cylinder, 3 c.c. of zinc iodide-starch solution and 1 c.c. of dilute sulphuric acid added, and the coloration compared with the standards. The intensity of the coloration is entirely dependent on the duration of the reaction, and it is therefore advisable for each observer first to ascertain the time necessary, in minutes, for the coloration produced by a normal nitrite solution to correspond with the shades of the colour scale; this time must then always be kept to in making the test. If a strong blue coloration is formed at once, the liquid must be correspondingly diluted; if the reaction does not occur in from five to six minutes, the amount of sulphuric acid is increased by 2 c.c. and another observation made after a few minutes.

Nitrites can also be determined colorimetrically by the meta-phenylenediamine method (*cf.* p. 407), or by means of sulphanilic acid and α-naphthylamine (*cf.* p. 408).

D. Nitric Nitrogen. Little importance is attached to the qualitative detection of nitric acid, in judging the character of an effluent, as the quantitative estimation of the amount present is essential. The qualitative tests are described in the section on Drinking Water and Water Supplies, p. 404.

It is often of value, however, to obtain quickly an approximate

[1] Thresh and Beale, *The Examination of Water and Water Supplies*, p. 564.

idea of the quantity of nitrate present, and this can be effected by a method first worked out by J. Horsley[1] and subsequently brought into practical use by F. W. Stoddart. The following description of the method is given by G. McGowan:[2]—

Ten c.c. of the sample, filtered from all suspended solids, is poured into a test-tube of rather thick glass (a bacteriological test-tube 15 cm. long by 1·25 cm. diameter), about 0·2 g. of pyrogallol added, and the solution shaken till uniform; after the first two or three trials it is unnecessary to weigh the pyrogallol, as it can then be measured out with sufficient accuracy. Two c.c. of concentrated, nitrate-free sulphuric acid is then allowed to flow slowly from a small pipette, plugged at the upper end with a piece of cotton-wool, so that the acid forms a layer below the water. Before withdrawing the pipette, its upper end must be closed by the finger, to prevent the acid still remaining in it from mixing with the aqueous layer of liquid. About 0·1 g. of pure, dry, powdered sodium chloride (the weight of which can also be judged after one or two trials) is then dropped into the tube, and falling—as much of it does—on the junction of the sulphuric acid and the water, it gives rise to a brisk effervescence. Should nitrate be present, a purple band is formed at the junction of the two liquids, the intensity of which is proportional to the content of nitrate.

A preliminary trial gives a rough idea of this amount, after which a second estimation is made along with three other simultaneous determinations with similar volumes of standard potassium nitrate solution. Thus, if the preliminary trial shows that about 0·6 parts of nitric nitrogen are present per 100,000 parts of liquid, the three standards are made to correspond to 0·4, 0·6, and 0·8 parts. In this way the nitric nitrogen in the sample may be gauged to within about 0·25 parts per 100,000. It is essential that the determinations should be carried out at the same time in both sample and standards, as it is useless to compare two tubes unless they have been prepared within a few minutes of one another; further, the sodium chloride used must be dry and finely powdered. There is considerable saving of time, in carrying out this test, if a number of dilute standard solutions of nitrate are always kept ready in stoppered bottles.

For the accurate quantitative determination of nitric acid the zinc-copper couple method (p. 404) and the phenol-sulphonic acid method (p. 405) have proved of value.

E. Suspended and Dissolved Organic Nitrogen and Ammoniacal Nitrogen. Samples of 200 c.c. each, of the filtered and of the unfiltered water, or larger quantities if the water is poor in nitrogenous matter, are heated in hard glass Jena flasks of 500 to 600 c.c. capacity with acid

[1] *Chem. News*, 1863, 7, 268.

[2] *Reports of the Royal Commission on Sewage Disposal*, 1904, Vol. IV., Part V., p. 23.

sodium sulphite, ferrous chloride, and a few drops of sulphuric acid, and boiled down to 10 to 20 c.c.; this treatment destroys the nitric acid. The residue is then treated with 20 c.c. of concentrated sulphuric acid and the nitrogen determined by Kjeldahl's method. The difference between the nitrogen contents of the unfiltered and filtered water gives the amount of suspended nitrogen, and the nitrogen content of the filtered water, the amount of organic and ammoniacal nitrogen present in solution (*cf.* p. 471).

F. Combined Organic Nitrogen. (*Albuminoid Nitrogen*). The amount of so-called albuminoid nitrogen is given by the difference between the organic and ammoniacal nitrogen found according to *E* and the ammoniacal nitrogen. For the direct determination the methods of Wanklyn, Chapman, and Smith (p. 417) are used.

8. Sulphuretted Hydrogen and Sulphides

Small quantities of sulphuretted hydrogen are best determined colorimetrically. For this purpose 100 c.c. of the water is treated with 1 c.c. of sodium nitroprusside solution (2 g. per litre) and the violet coloration which is formed compared with a standard scale of colour, each shade of which represents a definite amount of hydrogen sulphide (*cf.* p. 440).

The titration of hydrogen sulphide with iodine solution is not a reliable method for water containing much organic matter, but an approximate result may be obtained by this method by first determining approximately how much iodine solution is necessary to give a blue coloration with 200 c.c. of the sample. The volume of iodine solution required in this preliminary estimation is placed in a flask, 200 c.c. of the water introduced, the whole well shaken, starch solution added, and then more iodine solution, until the blue coloration is obtained.

Free hydrogen sulphide is best determined by passing air, freed from carbon dioxide by sodium hydroxide solution, through the water and absorbing the hydrogen sulphide carried off by the air, in lead acetate and determined in the usual manner; or, the air containing hydrogen sulphide is passed into *N*/100 iodine solution and the excess iodine titrated. The soluble sulphides are determined in the residue by treating it with a solution of zinc acetate and acetic acid and weighing as zinc sulphide, or by oxidising to sulphuric acid and weighing as barium sulphate; in the latter case, any sulphuric acid originally present must, of course, be deducted.[1]

[1] *Cf.* C. Weigelt, *Vorschriften für die Entnahme und Untersuchung von Abwässern und Fischwässern*, 1900, p. 20.

9. Chlorine

A. Combined Chlorine (Chloride). One hundred c.c. of the filtered water, or correspondingly less if the chloride content is high, is heated to boiling, treated with a little potassium permanganate, and the boiling continued until the manganese oxides separate in a flocculent condition and the supernatant liquid remains clear. Any excess of permanganate used is decolorised by addition of a little alcohol. The liquid is then filtered, the residue washed with hot water, and the filtrate and washings titrated with *N*/10 silver nitrate solution (*cf.* pp. 401 and 455). One c.c. *N*/10 silver nitrate solution = 0·003545 g. chlorine.

If much potassium permanganate has been used to oxidise the organic matter and the filtrate is alkaline, the chloride may either be determined as above, after neutralisation of the filtrate with nitric acid, or by preference gravimetrically, or by Volhard's volumetric method.

B. Chlorine in the Free State or as Hypochlorites (see p. 402).

10. Other Mineral Substances

Lead, copper, iron, zinc, manganese, calcium, magnesium, potassium, sodium, and sulphuric acid are determined according to the usual methods. If these constituents are present only in very small amounts, a correspondingly large quantity of the sample must be taken and previously concentrated, with addition of a suitable acid.

Phosphoric acid is determined by evaporating from 500 to 2000 c.c. of the water, according to the quantity present, to dryness in a platinum dish, fusing the dry residue with sodium carbonate and potassium nitrate, dissolving the melt in nitric acid, and precipitating the phosphoric acid from its nitric acid solution with ammonium molybdate.

11. Albuminoid Compounds, Sugar, Starch, and Yeast

The biuret reaction is the most suitable for detecting the presence of albuminoid compounds in effluents. The sample is treated with very concentrated sodium hydroxide solution and a few drops of a one per cent. solution of copper sulphate; in the presence of albuminoid compounds a reddish violet coloration is obtained.

Albuminoid substances can also be detected by means of Millon's reagent, which consists of a solution of one part of mercury in two parts of nitric acid of sp. gr. 1·42 diluted with twice its volume of water; it gives a rose-red coloration. In employing this test, the sample is concentrated (after first saturating with carbon dioxide if calcium is present, and precipitating any hydrogen sulphide with lead acetate), and then treated with the reagent at 60°. B. Proskauer[1] recommends the removal of hydrogen sulphide by shaking with litharge and then testing for

[1] Weigelt, *loc. cit.*

albumin by the biuret reaction or with potassium ferrocyanide and acetic acid; the precipitate must also always be tested for undissolved albumin. In presence of albuminoid compounds which are precipitated by lead salts very little lead acetate is used, the whole warmed, the precipitate washed and digested with pepsin in a 0·5 per cent. solution of lactic acid; the liquid is then tested by the biuret reaction.

Effluents are tested for sugar, after concentration, either with Fehling's solution or by the ring test with α-naphthol and concentrated sulphuric acid; the violet coloration obtained is a quick and delicate qualitative test. Starch and yeast are detected with the microscope after centrifuging the sample.

12. Oxygen

The method of L. W. Winkler is very suitable for the estimation of dissolved oxygen in water. Details of this method are given on p. 433.

The Adeney apparatus described on p. 431 is designed for investigating the changes in composition of the dissolved gases, due to fermentation of the organic matter, in mixtures of sewage and water.

F. Scudder uses a solution of indigo-carmine reduced by sodium hydro-sulphite in an apparatus designed to retain the reduced solution in an atmosphere of hydrogen. This solution can be used as a test for the presence of dissolved oxygen in mixtures of the sample under investigation with varying volumes of aerated water, after incubation for a defined period.[1]

13. Organic Carbon

The amount of potassium permanganate necessary for oxidation is no exact measure of the amount of organic matter present in water. Not only do the different organic compounds which may be present need varying amounts of oxygen for oxidation, but in addition inorganic compounds, such as ferrous salts, nitrites, and sulphur compounds, which occur fairly often in effluents, absorb part of the oxygen of the permanganate. A trustworthy method for the estimation of organic carbon has been worked out by J. König[2] from the one devised by P. Degener.[3] It is based on the conversion of all the carbon of the organic compounds into carbon dioxide by oxidising agents after removal of pre-formed carbon dioxide, the carbon dioxide thus formed is absorbed by alkali and weighed.

A. Organic Carbon in the Filtered Sample. Five hundred c.c. of the sample, if turbid, is quickly filtered through a large porcelain or metallic

[1] For details and apparatus, see Ministry of Health pamphlet on *Methods of Chemical Analysis*, 1929.

[2] *Z. Unters. Nahr. u. Genussm.*, 1901, 4, 193.

[3] *Z. Ver. deut. Zuckerind.*, 1882, 32, 59.

Gooch crucible of about 100 c.c. capacity, fitted with asbestos, and the drained residue washed with distilled water. The filtration of liquids which do not filter well, may be assisted by precipitation with a solution of iron or aluminium alum and disodium phosphate without affecting the results. The filtrate is placed in the round-bottomed flask *k*, Fig. 82, together with 10 c.c. of dilute sulphuric acid, and the flask connected with the condenser, but not with the other parts of the apparatus. The water is then boiled for half an hour, with open condenser and continuous condensation, until all pre-formed carbon dioxide has been expelled. It is then allowed to cool and 3 g. of
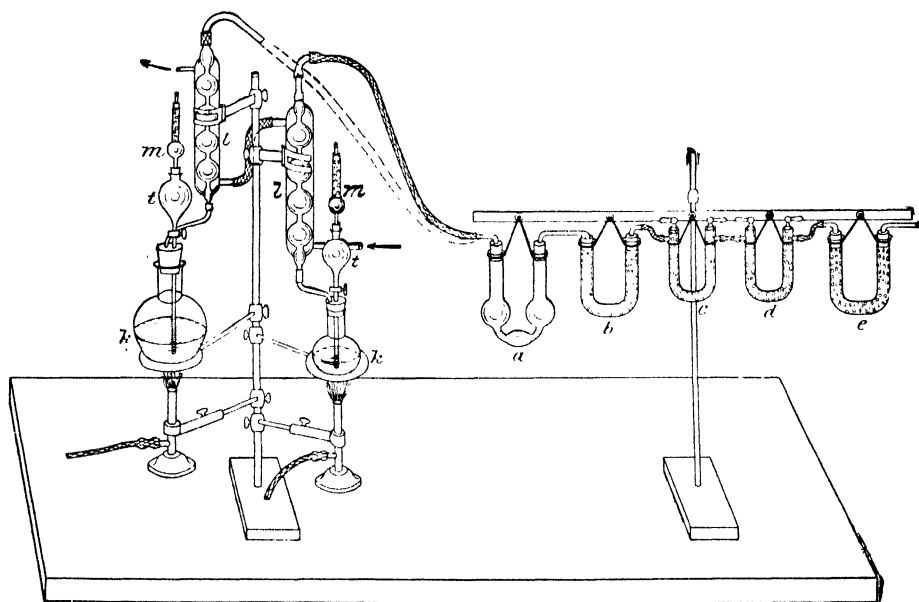
Fig. 82.

potassium permanganate, 10 c.c. of a 20 per cent. mercuric sulphate solution, and a further 40 c.c. of dilute sulphuric acid are added; the flask is then again attached to the condenser, and the latter connected up with the absorption tubes as shown in the figure. The Peligot tube *a* is filled up to the bottom of the bulbs with about 20 c.c. of concentrated sulphuric acid; tube *b* contains calcium chloride, *c* and *d* soda-lime, and *e* half soda-lime and half calcium chloride. The flask *k* is closed with a double-bored rubber stopper, which carries a glass tube leading to the condenser, and a dropping-funnel *t*, provided with a soda-lime tube *m*. The condenser retains the bulk of the water vapour which is formed, and the tubes *a* and *b* absorb the last traces; the tube *e* prevents access of water vapour and of carbon dioxide from the air. The tubes *c* and *d* serve to absorb the carbon dioxide formed by

the oxidation, and are weighed before and after the experiment. Strong potassium hydroxide solution may also be used to absorb the carbon dioxide, but it has the disadvantage that loss by spirting may occur should the liquid in the flask bump, which often happens during the oxidation of colloidal matter. After connecting up the apparatus, the flask *k* is warmed with a small flame in such a manner that bubbles of gas are slowly and uniformly evolved. When after boiling for some time, the evolution of gas ceases and the liquid in the tube *a* begins to suck back, the flame is removed for an instant from the flask *k*, an aspirator connected to *e*, the tap of the dropping-funnel *t* opened, and air drawn slowly through the apparatus until all the carbon dioxide has been removed; this takes about half an hour. Whilst air is being drawn through the apparatus, the contents of the flask *k* may be kept gently boiling by means of a small flame, in order to assist the expulsion of the carbon dioxide from the flask and condenser, care being taken that the condensation is efficient. The tubes *c* and *d*, which are provided with glass stopcocks, are removed at the end of the determination, closed, placed aside for half an hour, opened momentarily, closed, and weighed.

Volatile organic compounds behave similarly to carbon dioxide, and are not condensed with the water vapour; should they be present, therefore, too little organic carbon would be found. In such samples the pre-formed carbon dioxide and the organic carbon are determined together, by the initial addition of sulphuric acid, permanganate and mercuric sulphate. The pre-formed carbon dioxide is then determined separately in an equal volume of sample and the organic carbon found by difference.

B. Organic Carbon in the Suspended Matter. The residue left on the filter from the filtration of the sample is treated together with the asbestos filter, in a similar flask *k*, Fig. 82, of about 250 c.c. capacity, with 10 c.c. of 20 per cent. mercuric sulphate solution, and 5 g. of chromic acid or 10 c.c. of a 50 per cent. chromic acid solution, and the flask connected with the condenser and the absorption tubes; 50 c.c. of concentrated sulphuric acid is then added through the dropping-funnel *t*, a good flow of water being meanwhile maintained in the condenser, and the flask warmed, at first with a very small, and finally with a large flame, until no more gas passes through the Peligot tube. An aspirator is then attached, a slow current of air drawn through, and the determination continued as described under *A*.

Should the suspended matter contain calcium or magnesium carbonate, it must be boiled with dilute sulphuric acid before adding the chromic acid.

Fowler and Clifford[1] found that the above described moist com-

[1] *J. Soc. Chem. Ind.*, 1914, 33, 815.

bustion process could not be relied upon completely to oxidise resistant sewage residual products, for which the ordinary copper oxide combustion method is preferable.[1]

14. Carbonic Acid

The determination of pre-formed carbon dioxide may be carried out according to J. König's method as described under 13. The flask *k*, Fig. 82, is then connected through the condenser with the absorption tubes from the start, and the tubes *c* and *d* are weighed before and after the decomposition with sulphuric acid only.

The detection and quantitative estimation of carbon dioxide are carried out as described on p. 410.

15. Detection of Excreta

Animal excreta and products of animal and vegetable decay always contain small quantities of phenol, cresol, skatole, indole, and other compounds, which give intensely yellow coloured compounds with diazo-compounds, such as diazo-benzene sulphonic acid. P. Griess has based the following method for detecting these substances on this reaction: 100 c.c. of the water is treated in a cylinder of colourless glass with a little sodium hydroxide solution and a few drops of a freshly prepared solution of diazo-benzene sulphonic acid; if animal or vegetable products of excretion or decay are present, a yellow coloration appears within five minutes. For comparison, 100 c.c. of distilled water is similarly treated. Human urine is said to give a distinct yellow coloration at a dilution of 1 in 5000, and horses' urine at a dilution of 1 in 50,000.

To detect urea, which is only present in very fresh effluents, 100 c.c. of the liquid is boiled with a few drops of acetic acid, filtered, evaporated to dryness, extracted with alcohol, the alcohol evaporated off, the residue dissolved in water, the solution evaporated down to 3 c.c. and then acidified with nitric acid; if urea is present twinned crystals of urea nitrate are formed on evaporation.

Dung particles may be detected in the sediment of a water by microscopic examination. A simple test for recent fæcal pollution is to warm a few c.c. of the liquid with an equal volume of strong sulphuric acid; a pink coloration indicates skatole.

It is not, however, usually possible to detect these products of excretion and decay directly, and pollution from these sources can

[1] W. E. Adeney and Miss B. B. Dawson have studied the action of acid bichromate upon various organic compounds and upon sewage with a view to determining the total oxidisability of sewage and other polluting liquors. A known volume of the sample is digested with an excess of potassium bichromate and sulphuric acid, and the residual bichromate remaining at the end of the reaction titrated by means of ferrous sulphate. (*Proc. Royal Dublin Soc.*, 1926, **18**, 199; "The Dilution Method of Sewage Disposal" (*loc. cit.*), p. 130 *et seq.*

only be deduced indirectly from the presence of a large amount of nitrogenous organic matter (or, as this is easily decomposed, of nitric nitrogen), of sulphur or sulphates, and of carbon or carbonates. As such refuse is also rich in chlorides, the chlorine content affords a further guide as to their presence. Even if the water is found to contain a large amount of any one of these substances this may be caused by the natural conditions; but if these compounds are present simultaneously in large amount, it is safe to conclude that pollution has occurred, especially if they are not contained to the same extent in other waters from the same locality.

16. Detection of Coal Gas Products

Contamination with coal gas products may occur through leakage from the mains. They are detected, according to C. Himly, by mixing a large quantity of the water with chlorine water, exposing the mixture to sunlight, and removing the excess of chlorine by agitation with mercuric oxide; if coal gas is present a strong smell of ethylene dichloride or of similar chlorinated hydrocarbons is observed. H. Vohl infers pollution by gas or tar water from the presence of ammonium sulphide or of ammonium carbonate, sulphate and thiosulphate, or from increased amounts of the corresponding calcium and magnesium salts. Phenol should also be tested for; if present, a violet coloration is produced by ferric chloride, a yellowish-white precipitate of tribromophenol bromide by bromine, and rosolic acid is formed on heating with oxalic and sulphuric acids. It is also advisable to test for thiocyanates with ferric chloride, as these are present in ammonia recovery liquor, which is often discharged into the sewers.

17. Tests for Putrescibility: Fermentation Experiments on Effluents

The view that a sample which keeps clear for five or more days without undergoing putrefaction can be passed as satisfactory does not always hold good. For instance, a perfectly clear sample may be prepared by the addition of an excess of lime which may be kept for a long time in well-closed bottles without putrefactive bacteria making their appearance, as free lime hinders their development. If the same liquid is kept in open vessels the free lime is gradually neutralised by carbon dioxide, and putrefactive bacteria then appear and decompose the soluble organic matter, but without producing any smell of putrefaction. If, however, a similar effluent containing a large amount of free lime flows into a slow-flowing river, the formation of mud is not improbable, and unpleasant smells may then be produced, especially in warm weather.

Although, therefore, tests on the putrescibility of effluents have usually little practical bearing, they sometimes allow of conclusions as to the greater or lesser potential oxygen demand by the contained organic matter, and consequently the harmfulness of the effluent.

The following methods are adopted in testing the putrescibility of an effluent:—

(*a*) Two bottles, each containing ½ to 1 litre of the sample, are allowed to stand uncovered.

(*b*) Two bottles, containing the same quantities as in *a*, are closed with sterilised cotton-wool.

(*c*) Two bottles, also containing the same quantities, are kept well-stoppered.

One of each of these pairs of bottles is kept at a low temperature, 0° to 10°, and the other at 10° to 20°.

If the liquid contains free lime, a further pair of bottles is filled with the sample, in which the lime has been previously neutralised with carbon dioxide, and is then treated in the same manner as the others.

If it is necessary to dilute the liquid, this is done with distilled water which has been boiled for some time and then cooled, the vessel being meanwhile closed with a plug of cotton-wool.

If the effluent contains no putrefactive bacteria, a further series of bottles are equally inoculated with any liquid which is in a state of putrefactive fermentation.

The separate samples are then examined after a fixed time, microscopically, bacteriologically, and also chemically, for ammonia, nitrous acid, hydrogen sulphide, oxygen-absorbing power with permanganate, total nitrogen, colour, smell, etc.

The incubator test described on p. 470 may also be employed, or a mixture of one volume of the sample with, say, nine volumes of tap water is submitted to incubation in a completely filled and closed bottle for several days, and the loss of oxygen noted. (*Cf.* also Adeney's experiments, p. 438.)

The loss of dissolved oxygen on incubation in this way has been made the basis of a standard of comparison for effluents by the British Royal Commission on Sewage Disposal in their Eighth Report, 1913. According to the Commission an effluent may be considered satisfactory if as discharged it contains not more than 3 parts per 100,000 of suspended matter, and with its suspended matter included does not take up at 65° F. (18·3° C.) more than 2·0 parts per 100,000 of dissolved oxygen in five days.

MICROSCOPIC AND BACTERIOLOGICAL EXAMINATION

The microscopic and bacteriological examination of effluents is essentially the same as that of drinking water. (*Cf.* pp. 442-49.) The occurrence of *Beggiatoa* and of *Leptomitus* demand special attention in effluents containing more or less albuminoid matter, such as those of breweries, sugar, starch, and paper factories, etc. *Beggiatoa* occurs under the inflow of effluents into brooks and rivers in thick slimy growths which cover stones, wood, and other materials in the water; they are composed of countless, fine, non-branching threads which, in the riper stages of development, contain varying quantities of embedded, sulphur-coloured grains. Alcoholic solutions of aniline dyestuffs, sodium sulphite, etc., show up the structure of the threads, which are articulated into long and short rods and, in older threads, into discs and coccæ. The fungus *Leptomitus lacteus* covers the bed of the stream with a greyish-white slime; it differs from *Beggiatoa* by the threads showing both branches and constrictions, and should be distinguished from *Sphaerotilus natans*, which is characteristic of pollution with crude sewage.

CRITERIA OF THE CONTAMINATION DUE TO EFFLUENTS AND THEIR INJURIOUS EFFECTS

In examining the contamination of a stream due to the effluents from a works or factory, the sample must be collected at the point where a possible injurious effect is suspected, as otherwise, in consequence of self-purification, the water may subsequently lose its specific deleterious character. The use for which the water in question is destined must also be borne in mind, because the injurious effects of the constituents of effluents act harmfully in very various ways according as to whether the water is employed for fish culture, drinking supply for cattle, industrial purposes, agricultural purposes (for soil and vegetation), etc.; a water which is injurious for one purpose may be quite harmless for another.

1. Effects on Fish Culture

The fact that fish have died in a stream polluted by an effluent cannot in itself be considered as a proof of the injurious character of the effluent, as extensive illness or mortality amongst fish are on record which were due to natural diseases and not to pollution. The following methods are available for determining the injurious effect of an effluent or of the water of a stream contaminated thereby.

A. By Examination of the Fauna and Flora of the Contaminated Water. Natural waters in which fish are to live must contain a sufficient quantity of animals and plants for their food. According to

the degree and kind of the contamination, the animal and vegetable life of the water may either be totally destroyed, or its development hindered, or it may be changed in character. Comparison with neighbouring parts of the same waters, as similar as possible but not liable to contamination from the same source, may considerably simplify the investigation in this respect. More specific inquiries on this aspect of the pollution necessitate an expert zoological and botanical examination.

B. By Examination of the Fish. When the water is contaminated by either copper, zinc, lead, iron, arsenic, or dyestuffs, etc., an examination of the fish may prove helpful. Fish sent for examination should be wrapped singly in parchment paper and packed in ice and straw. Either the whole fish, or the flesh and the intestines separately, are tested for the suspected injurious substances by the ordinary toxicological methods.

C. By Examination of the Water and by Experiments on its Injurious Effect on Fish. The examination of the water is especially necessary when several effluents of varying character participate in the contamination, or when the constituents of the effluent alter on standing. Effluents which contain large amounts of organic matter, such as town effluents and effluents containing fæces, may be quite harmless to fish when fresh, and in fact some fish often frequent, by preference, the places where such effluents enter the stream; when, however, the organic matter of such effluents putrefies, the water may become injurious to fish in consequence of deficiency of oxygen, or of the formation of hydrogen sulphide, ammonia, etc. The limiting figures which have been found by experiment for the individual injurious constituents cannot, and should not, be considered as applicable in all cases, but only as giving a general idea. C. Weigelt[1] has called attention to the fact that not only are the various species of fish affected differently by any one harmful ingredient, but also that the effect varies with the same species when of different weight and age. The temperature has also an influence, the harmful effect of any ingredient usually rising and falling with the same. Frequently it is not possible to come to any final conclusion from the recorded results for the limiting amounts of the individual injurious constituents, and it is then necessary to make direct experiments, either with the contaminated water or with the contaminating substances.

The following limiting quantities for various harmful substances were obtained by Haselhoff[2] as the result of direct experiments at the experimental station at Münster. The experiments were performed with carp, tench, and goldfish; the figures always refer to 1 litre of

[1] *Landw. Versuchs-Stat.*, **28**, 321; *Archiv. f. Hyg.*, 1885, **3**, 39.
[2] *Landw. Jahrbuch*, 1897, **26**, 76; 1901, **30**, 583.

water, and indicate, unless otherwise noted, the point at which the fish became ill or died.

1. *Oxygen Content:* Fish thrive unharmed on 2·8 c.c., *i.e.* about $\frac{1}{3}$ of the amount of oxygen usually present in flowing water. The effect of a deficiency of oxygen in putrefying water is associated with other changes, including the formation of the substances 2 to 5, which may have an injurious effect.

2. *Hydrogen Sulphide:* 8 to 12 mg.

3. *Free Carbon Dioxide:* 190 to 200 mg.

4. *Free Ammonia:* 17 mg. for small, and 30 mg. for large fish.

5. *Ammonium Carbonate:* 170 to 180 mg. $(NH_4)_2CO_3 + 2NH_4 \cdot HCO_3 =$ 36 to 38 mg. ammonia.

6. *Ammonium Chloride:* 0·7 to 1·0 g.

7. *Ammonium Sulphate:* 0·7 to 1·0 g.

8. *Sodium Chloride:* 15 g.

9. *Sodium Carbonate:* 5 g.

10. *Calcium Chloride:* 8 g.

11. *Magnesium Chloride:* 7 to 8 g.

12. *Strontium Chloride:* 145 to 172 mg.; this limit can be raised to 181 to 235 mg. if the quantity added to the water is increased gradually.

13. *Barium Chloride:* In individual cases 20·3 mg. acted injuriously whereas in others 64·3 to 500 mg. produced no effect; fish seem to be very variously affected by barium chloride and to be able to accustom themselves to it to a certain degree.

14. *Zinc Sulphate:* 31 mg. ZnO = 110 mg. $ZnSO_4$. The fine, flocculent zinc hydroxide which is separated exerts an additional injurious effect by settling on the gills and affecting respiration.

15. *Copper Sulphate:* 4 mg. CuO = 8 mg. $CuSO_4$; smaller amounts may act injuriously in course of time.

16. *Ferrous and Ferric Sulphates:* The injurious action of these salts varies with the amount of flocculent ferric hydroxide which separates; the experiments showed an injurious effect with 40 to 50 mg. of ferrous sulphate. C. Weigelt observed no injurious effect with 50 mg. of ferrous sulphate, but found that 15 to 30 mg. of ferric sulphate was deleterious.

17. *Free Lime:* 23 mg. CaO.

18. *Free Sulphuric Acid:* 35 to 50 mg. SO_3.

19. *Sulphurous Acid:* 20 to 30 mg.

20. *Free Hydrochloric Acid:* 50 mg.

21. *Potassium Alum:* 300 mg. $K_2Al_2(SO_4)_4 + 24H_2O$.

22. *Chrome Alum:* 230 mg. $K_2Cr_2(SO_4)_4 + 24H_2O$.

The deleterious action on fish of a number of different dyestuffs was also investigated.[1]

[1] Cf. *Landw. Jahrb.*, 1901, **30**, 583.

2. Injurious Effect on Live Stock

Water should be as pure for cattle as for human beings, although cattle may be less susceptible to the injurious effects of impurities in the water. In particular, impurities in the drinking water of milch cows may act injuriously, as the composition of the milk may be adversely affected; abortion may be caused in pregnant animals through pollution of the drinking water with putrid matter or with purgative salts such as chlorides, sulphates, or nitrates, in considerable quantity; horses may develop colic from the same causes, etc.

Water contaminated by effluents containing poisonous substances such as lead, copper, zinc, arsenic, etc., may spoil herbage when meadows or fields are flooded, either by mechanical adhesion of these impurities to the plants or by absorption; in either way the health of the stock consuming such fodder may be injuriously affected. These poisons are detected in the fæces, and under certain circumstances in the urine; and in dead animals, in the remains of food in the stomach and intestines.

3. Injurious Effect for Industrial Purposes

Any water which is turbid or which is strongly contaminated by sludge, dyestuffs, or mineral matter, must be rejected for industrial and technical purposes.

In feed water for boilers it is necessary to distinguish between substances which actually attack and destroy the boiler plates, and those which cause the formation of boiler incrustation and thus hinder the conduction of heat. To the first category belong free acids, ammonium salts, magnesium chloride, much dissolved oxygen, humus substances, and grease (from machine oils); molasses have also been found to be injurious to the boilers in sugar factories. According to the investigations of Fischer, the formation of boiler scale is due to calcium sulphate, calcium carbonate, and magnesium carbonate. This question is fully dealt with in the section on Feed Water for Boilers p. 454.

Water for paper mills, dye works, print works, bleach works, and glue works must be soft and especially free from iron.

Sulphates, alkali carbonates, and especially nitrates, actively assist the formation of molasses, and waters containing these substances cannot therefore be used in sugar works.

In all fermentation industries, especially breweries and distilleries, perfectly pure, clear, and soft water is required. The water must, above all things, be free from products of decay, and must contain as few micro-organisms as possible, as these cause subsidiary fermentations which may adversely affect the aroma and taste of the products.

Such water must also be rejected for use in dairies, as vessels cleaned with it retain micro-organisms which injuriously affect the separation of curd; also, butter which has been washed with such water soon becomes rancid and bad.

4. Injurious Effect on the Soil

An effluent, or a brook contaminated by an effluent, may affect the soil injuriously in three ways. If the water contains much suspended matter, such as iron oxide mud, particles of cinder, slag, or charcoal, organic fibres, etc., these substances may clog the soil, either by forming a thick layer on the surface and choking the normal vegetation, or by stopping up the pores in the soil, thereby causing it to become acid, and thus injuriously affecting the vegetation.

An effluent may also convey substances to the soil which are either directly injurious to plants, such as ammonium thiocyanate, arsenious acid, metallic oxides, etc., or which are converted by oxidation into injurious substances—for instance, sulphur compounds.

Finally, free mineral acids, sodium, calcium and magnesium chlorides, and ferrous, copper, and zinc sulphates and nitrates, exert a solvent action on the constituents of the soil, when carried to meadows or fields by an effluent, so that after they have acted for some time the soil becomes steadily poorer in calcium, magnesium, and potassium, and, after a longer or shorter period, according to the original fertility, the crops become poorer. In consequence of this solvent action on nutrient constituents, the productiveness of the soil may at first be actually improved ; hence it is often concluded that such waters are not harmful, but both practical experience and scientific investigations have fully established the harmful effect of such effluents. The metallic oxide of the sulphates remains behind in the soil and may be absorbed by the plants. The chlorides, moreover, effect a closer packing of the soil particles, which makes the ground heavy and therefore less fertile.

In determining whether a soil has suffered injury from effluents, it is therefore necessary, not only to estimate the amount of the injurious substance in the soil and in the vegetation growing on it, but also the contained calcium, magnesium, and potassium, and the looseness of the soil particles, in comparison with those of a similar soil which has not been affected by the effluent. The action of a certain type of effluent is sometimes indicated by the character of the vegetation; for instance, the occurrence of *Arabis Halleri* or *Petraea* is characteristic for soils which have been damaged by zinc compounds, and *Atriplex hastata* for those which have been spoilt by common salt.

The sampling and examination of the soil is carried out as described in the section on "Soils," pp. 588, 592.

5. Injurious Effect on Plants

The action of injurious effluents on plants cannot always be proved by an examination of the plants themselves, as some injurious substances, such as ammonium thiocyanate, very soon undergo change by vegetable metabolism. Other injurious substances, such as arsenious oxide, are only absorbed in very minute amount, but a large number, especially metallic chlorides and sulphates, are absorbed by the plants in considerable quantities.

6. Injurious Action on Ground and Well Waters

If the composition of a ground or well water has been affected by an effluent soaking into the soil, the characteristic constituents of the effluent, or the products of their interaction with the constituents of the soil, should be capable of detection in the water. When this is suspected it is advisable to also collect samples of the ground water along the line of communication between the source of contamination and the contaminated well, as the examination of such samples may be helpful in drawing conclusions with regard to any effect of the effluent on the well water.

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FERTILISERS

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DRAWING OF SAMPLES

BEFORE proceeding to discuss analytical methods, it appears relevant to refer to the necessity for due care in drawing samples so that they may be as fairly representative as possible of the bulks from which they are taken. Many fertilisers are not homogeneous in composition, and unless due care is taken to ensure as nearly as possible a truly average representation of the bulk concerned, the results of the analyst, however correct they may be as regards the samples submitted to him, may, nevertheless, be unfair to the buyer or to the seller. Experience indicates that this point cannot be too strongly stressed. The majority of analysts probably have no control over the drawing of the samples which they are called upon to analyse, and may often be blamed for discrepancies between their own and other analyses where the differences are really due, not to analytical variations, but to differences between samples. Some analysts, however, in addition to their own laboratory work, make themselves responsible for undertaking or directing the drawing of samples; and it happens sometimes that even those who do not undertake this work are consulted about sampling.

Under the old Fertilisers and Feeding Stuffs Act of 1906, the Ministry of Agriculture exercised powers of direction as to the drawing of samples intended for investigation under the provisions of the Act, and in the new Fertilisers and Feeding Stuffs Act of 1926 (which came into operation in 1928), the official regulations as to sampling have been extended and modified by the Ministry with the advice and assistance of a committee which, in addition to agricultural analysts, comprised a number of experienced representatives of the various branches of trade and manufacture connected with the commodities coming within the purview of the Act. As these regulations were the result of careful deliberation, they may be here reproduced as indicative of the most recently approved methods of sampling, although, of course, no method of sampling can altogether eliminate chance effects due to lack of uniformity in the hundreds, or possibly thousands, of packages that may sometimes be contained in a single consignment.

Manner of Taking Samples

(*Extracted from the Fertilisers and Feeding Stuffs Regulations*, 1928)[1]

In the case of a Fertiliser—

(i) When the fertiliser is delivered or prepared for delivery in bags or other packages, a number of bags or packages shall be taken as follows, viz.:—

	Number taken for sampling. Per cent.	But not fewer packages than
Where the quantity is from 2 to 20 packages .	20	2
Where the quantity is from 21 to 60 packages .	10	4
Where the quantity is from 61 to 200 packages .	7½	6
Where the quantity is from 201 to 500 packages .	5	15
Where the quantity is from 501 to 1000 packages	4	25
Where the quantity exceeds 1000 packages .	3	40

When the number of packages to be drawn according to the above percentage scale contains a fraction, this fraction shall be counted as a whole number.

In each case the quantity shall be treated as composed of separate approximately equal portions, the number of portions being reckoned as the same as the number of packages to be selected for the purpose of sampling, and one package shall be drawn by the inspector or official sampler at random from each of these portions.

Where the quantity exceeds 500 packages it may, in the discretion of the inspector or official sampler, be treated as composed of separate parcels of 500 packages each, any one of which may be sampled separately; but where two or more samples are taken under this provision from one quantity, they shall be mixed together to form one sample for the purposes of the Act.

Only unopened packages shall be selected for the purpose of the sample.

(ii) The sample shall be drawn by one of the following methods:—

(a) The selected bags or packages shall be emptied separately on a clean and dry floor and worked up with a spade and one spadeful from each set aside. The spadefuls so set aside shall then be thoroughly mixed together and any lumps broken up by the hand or spade. From this mixture a sample from about 2 lb. to 4 lb. in weight shall be taken.

(b) As an alternative method, when the material is of a suitable nature, a portion shall be drawn from each selected package by means of a suitable sampling spear; provided

[1] The Roman numerals and letters in brackets are retained to facilitate reference to the Regulations.

that, in the case of a sample taken by an inspector, a sampling spear shall not be used if objection is raised thereto, prior to the taking of the sample, on the grounds that the material is unsuitable. The separate quantities thus taken from the selected bags or packages shall be thoroughly mixed together and a sample from 2 lb. to 4 lb. in weight shall be taken from the mixture.

(iii) Where the fertiliser is in bulk and is in fine condition so that it will pass into a sampling spear pressed into it, it shall be sampled with the sampling spear, which shall be pressed into the bulk in different parts in such a manner that portions are withdrawn at random from different parts of the bulk.

The number of portions taken by the spear shall be as follows :—

	Portions.
Where the quantity does not exceed 1 ton . . .	4
Where the quantity is from 1 ton to 2 tons . . .	6
Where the quantity is from 2 tons to 5 tons . .	10
Where the quantity is from 5 tons to 10 tons . .	15
Where the quantity is from 10 tons to 25 tons . .	25
Where the quantity is from 25 tons to 50 tons . .	40
Where the quantity is from 50 tons to 100 tons . .	60

Where the quantity exceeds 50 tons, it may, in the discretion of the inspector or official sampler, be treated as composed of separate portions of 50 tons each or part thereof, and each of these portions shall be treated as separate for sampling purposes, as many portions being drawn, according to the scale above, as there are portions of 50 tons or part thereof. The portions withdrawn shall be thoroughly mixed together and a sample from 2 lb. to 4 lb. in weight shall be taken from the mixture.

(iv) Where the fertiliser is in a coarse or lump condition, as in the case of caustic or burnt lime, not ground, the sample shall be drawn as follows :—

(a) *In Bulk.* Four spadefuls shall be taken for each ton, each such spadeful to be taken at random from a different part of the lot. The quantity thus removed shall be crushed immediately and passed through a sieve with meshes 1¼ inch square. Any lumps and stones in the portion taken are not to be disregarded, but shall be broken up and mixed with the remainder of the sample. It shall be mixed thoroughly and rapidly and a sample of 4 lb. to 6 lb. taken.

(b) *In Packages.* The packages shall be selected according to the scale given in (i) and treated as described in (ii) (a). The spadefuls removed shall be crushed immediately and treated as in (iv) (a).

(v) Where the fertiliser consists of materials such as caustic lime or slaked lime (calcium hydroxide) which are liable to undergo change on exposure to air and moisture, or where the fertiliser consists of materials such as calcium nitrate or ammonium nitrate, which are liable to absorb moisture, or where the material is sulphate of ammonia, the sampling shall be carried out in a dry place and as expeditiously as possible, the division of the sample into parts (see paragraph D) shall be carried out at once, and each part shall be placed in a clean, dry, stoppered bottle or air-tight container. Care must be taken to see that the sample bottles or containers are completely dry before use.

(vi) When the fertiliser consists of bulky material, uneven in character and likely to get matted together, such as shoddy, wool refuse, hair, etc., the selected packages shall be emptied on a clean dry floor, or if in bulk, the portions selected at random from different parts of the bulk shall be placed on a clean dry floor, the matted portions torn up, and all the portions thoroughly mixed together. The sample shall be taken from the mixture and shall be from 2 lb. to 4 lb. in weight. If the material separates into a fibrous part and a powdery part, the sample drawn shall consist of these two kinds in approximately their relative proportions by weight, as they exist in the fertiliser.

Where the quantity of the whole consignment does not exceed 2 cwts., the sample may consist of such a portion of the consignment or bulk as is fairly representative of the whole, and the sample shall be of such a quantity that each of the parts into which (under paragraph D) it is to be divided will be not less than half a pound in weight.

In every case the sampling shall be done as quickly as is possible consistently with due care and the material shall not be exposed any longer than is absolutely necessary.

D. *Division of Sample.*

Where a sample has been taken with a view to the institution of any civil or criminal proceedings, the person taking the sample shall divide it into three parts, as nearly as possible equal, in the following manner :—

(xiv) (a) *In the case of dry or powdered substances.* The sample, drawn as prescribed in the foregoing section, shall be thoroughly mixed on heavy glazed paper or oilcloth and divided into three similar and approximately equal portions. Each such portion shall be placed in a separate tin or bottle of a kind described in paragraph (xv) and shall constitute a part of the sample.

(b) *In the cases of substances in a fluid or semi-fluid condition.* The sample drawn as prescribed shall be thoroughly mixed and at once divided into similar and approximately equal parts by pouring successive portions into each of three bottles.

(xv) Each of the parts into which the sample is divided shall be packed in a dry clean bottle or (except in the case of a fertiliser) a dry clean tin with close-fitting lid (such as a lever lid), so that the original composition of the fertiliser or feeding stuff may be preserved. In the case of caustic lime, slaked lime (calcium hydroxide), calcium nitrate, ammonium nitrate, ammonium sulphate and other substances likely to undergo change if not kept in an air-tight receptacle the bottle used shall have a ground-in stopper, or be provided with a metal cap with inner pad. Each of the said parts shall be so secured and sealed that the bottle or tin containing the sample cannot be opened without breaking the seal.

(xvi) Each of the said parts shall be sealed and initialed by the person taking the sample. It may also be sealed or initialed by the person on whose premises the sample is taken, or his representative. Each part shall be marked with the name of the article, any mark applied to the article in compliance with the Act, the date and place of the sampling, and with some distinguishing number, in such a manner that the particulars so marked can be seen without breaking the seal or seals.

(xvii) Samples shall not be drawn from parcels bearing the appearance of having received damage in transit or after delivery.

Preparation of Samples for Analysis.

The next step is to prepare the sample in a suitable condition for analysis. The directions of the Ministry of Agriculture, as laid down in the Fertilisers and Feeding Stuffs Regulations (1928), are as follows:—

(a) In the case of powdered fertilisers in a dry, or moderately dry, condition, the sample shall be passed through a sieve having apertures about one millimetre square.

Adventitious materials which cannot be conveniently crushed, *e.g.*, fragments of metal in basic slag, shall be removed and allowed for.

(b) Other substances which are dry enough to powder, but which are not in a fine condition, shall be pulverised until the sample passes through a sieve having apertures about one millimetre square.

(c) Wool, hair, hoof, shoddy and similar substances shall be pulled apart and cut until in a fine condition; or, if dry, they may be passed through a shredding machine.

(d) Moist fertilisers which do not admit of being passed through a sieve shall be thoroughly mixed by the most suitable means.

(e) In the case of substances which gain or lose water during the process of pulverising or mixing, the proportion of water shall be determined in the coarse and in the powdered condition respectively, and the results of the analysis of the powdered sample shall be calculated to the water content of the original coarse substance.

(f) Crystalline or saline materials, such as sulphate of ammonia, nitrate of soda or potash salts, may be prepared by being well mixed and rapidly ground in a stoneware mortar, the portion finally reserved for analysis being specially finely ground.

(g) When the sample has been passed through the sieve and thoroughly mixed, or, if not passed through the sieve, has been thoroughly mixed, a part of it not being less than 100 g. shall be placed in a stoppered bottle and from this the portions for analysis shall be weighed.

General Observations

Fertilisers may consist of materials in which the only element of fertilising value is nitrogen, such as sulphate of ammonia, nitrate of soda, calcium cyanamide, dried blood, horns, hoofs, hair, shoddy, etc.; or of fertilisers that are purely phosphatic, such as superphosphate, basic slag or ground mineral phosphate; or of fertilisers whose value lies only in their potash content, such as potassium sulphate, potassium chloride (known in trade by its earlier name of muriate of potash), kainit, and various indeterminate mixtures of naturally occurring potassium salts. On the other hand, there are fertilisers that yield both nitrogen and phosphates, such as various forms of bone manure, meat manure or fish manure, while some natural fertilisers like Peruvian guano contain all the leading elements of fertility. There is also the large class of artificial mixtures known as "compound fertilisers" which may contain nitrogen, phosphoric acid and potash in various forms.

The work of the agricultural analyst as regards fertilisers is to determine the percentages of nitrogen, phosphoric acid or potash, sometimes merely the respective totals, but sometimes with reference to the form in which they exist, or to their solubility or behaviour when treated with specified solvents.

I.—NITROGEN

A. Total Nitrogen

Prior to 1883, the agricultural analyst was wholly dependent for his nitrogen results upon the tedious soda-lime dry combustion process of Will and Varentrap and its modifications. Kjeldahl[1] then made the happy observation that in organic substances—that is to say, such organic substances as those occurring in fertilisers and feeding stuffs—it was possible to convert substantially the whole of the nitrogen into ammonium sulphate by boiling with concentrated sulphuric acid, after which, of course, the estimation of ammonia by distillation with sodium hydroxide was simple. The conversion was slow and not always complete, but was found by Kjeldahl to be hastened and complete reaction assisted by the addition of potassium permanganate. It was later found, however, that potassium permanganate was dangerous because if the quantity used was excessive, some of the ammonia formed might be oxidised and lost, presumably in the form of free nitrogen. For this reason the use of permanganate was ultimately abandoned though many workers persisted for years in its use. Wilfarth and Arnold found[2] that the addition of a drop of mercury, a little mercuric oxide or copper sulphate greatly hastened, by catalytic action, the oxidation of the organic matter and so shortened the time of digestion with acid.

In 1889 an important advance was made by Gunning,[3] who introduced the use of potassium sulphate as an addition to the sulphuric acid after the action of the acid had continued for a short time. The higher boiling-point of the solution greatly reduced the time of oxidation and many operators found that under these circumstances the addition of mercury or copper as catalyst was no longer necessary.

There is no doubt, however, that with many materials, the addition of a drop of mercury with the acid, followed later by Gunning's potassium sulphate (or sodium sulphate, which is now more frequently used), the complete destruction of the organic matter and complete conversion of the nitrogen into ammonium sulphate is more quickly accomplished than if the addition of mercury is omitted.

The writer of this section made in 1895 a critical survey of Kjeldahl's method, and its developments as applied to organic nitrogenous compounds of heterogeneous constitution.[4]

The process was further improved in 1886[5] by Jodlbauer, who

[1] *Z. anal. Chem.*, 1883, **22**, 366.
[2] *Chem. Zentr.*, 1886, **3**, 16, 17, 113, 337.
[3] *Z. anal. Chem.*, 1889, **28**, 188.
[4] *J. Chem. Soc.*, 1895, **67**, 811.
[5] *Chem. Zentr.*, 1886, **3**, 17, 433.

extended its application to mixtures containing nitrates by adding phenol to the sulphuric acid, whereby nitric nitrogen liberated by the sulphuric acid became fixed as a nitro-phenol. Zinc dust was added while the mixture was still cold, the nitric radicle being thereby reduced to the amido-form and subsequently, during digestion, to ammonia. Some operators have substituted salicylic acid for phenol; there is perhaps a manipulative convenience in this, but it has always appeared to the writer that phenol, having one more replaceable hydrogen atom than salicylic acid, may afford a more secure trap for the NO_2 group. Sodium thiosulphate is sometimes preferred to zinc dust as a reducing agent.

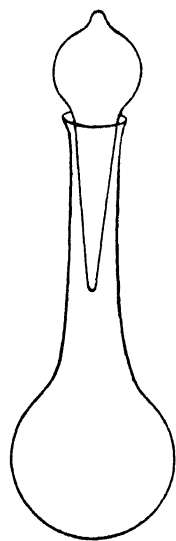
This "Kjeldahl-Gunning-Arnold-Jodlbauer" process in relation to these and some further modifications is discussed in detail in the paper referred to above.[1]

It is essential that the contents of the flask should be kept as cold as possible during the addition of the phenol-sulphuric acid, especially if ammonium salts are present as well as nitrates, otherwise there is apt to be a loss of nitrogen.

Further, the phenol sulphuric acid (or salicylic sulphuric acid) should not be added with a pipette, but should be added suddenly from a beaker or measure so as immediately to cover or "swamp" the dry fertiliser in the flask.

Fig. 83.

The further manipulative details will now be considered. The digestion should be carried out in a high resistance round-bottomed glass flask having a bulb capacity of about 200 c.c. Some operators use a flask with a very prolonged neck, on the inner surface of which volatilised sulphuric acid may recondense and flow back into the tube. The loss of acid is, however, much better prevented, allowing also the use of a flask with a shorter and broader neck, if there is inserted into the mouth of the flask a loosely-fitting hollow blown glass stopper, the lower end of which is extended to a length of about 3 inches tapered nearly to a point, while the head forms a bulb which loosely stoppers the orifice of the flask while the length of the lower end keeps it balanced. The writer has been in so many laboratories where this very simple and most useful device (first recommended by Kreusler) is not in use that it seems desirable to supply the accompanying illustration (Fig. 83).

In a fertiliser in which the absence of nitrates has been primarily ascertained, a suitable quantity, which may vary from about 1 g. to as much as 6 g. (according to the nature of the material and the

[1] B. Dyer, *J. Chem. Soc.*, 1895, 67, 811.

percentage of nitrogen contained), is introduced into the flask with one drop of mercury; 20 c.c. of concentrated sulphuric acid, or more if required, is then poured in and the contents of the flask mixed by gentle rotation, the loose stopper being inserted. A small piece of paraffin wax should be added to prevent excessive frothing.

The flask is placed in a sloping position over a small gas jet, the heat being preferably localised by the interposition of a sheet of metal or asbestos having a circular hole, which allows a considerable portion of the bulb of the flask to be strongly heated without allowing the flame to play upon the area of the flask above the liquid. This precaution obviates possible decomposition of ammonium sulphate in case an increase in the pressure of the gas should cause an unanticipated expansion of the flame.

There are various forms of apparatus for holding the Kjeldahl digestion flasks side by side and for controlling and regulating the gas supply thereto attached, which may be seen figured in the catalogues of any of the leading makers of chemical apparatus, so they will not be described here.

After the initial action of the heated acid upon the material has abated, the loose bulbed stopper is withdrawn for a few moments (being carefully held in the hand and not allowed to drip), and 10 g. of potassium sulphate or of anhydrous sodium sulphate is shot into the flask, the stopper being then replaced and the digestion continued until such time as the fluid is colourless or nearly so.

The nitrogen of some materials, such as powdered hoofs and horns, is only slowly converted to ammonium salt, even with the aid of mercury, and in such cases it is well to continue a gentle heating of the flask for even an hour after the operation appears to be complete. If this precaution of extra long heating is neglected, results for hoof or horn may easily be obtained too low—to the extent of as much as 0·2 per cent. With such materials the time of total digestion should extend to four hours.

For fertilisers containing an admixture of nitrates, 30 c.c. of sulphuric acid is used. One uses in place of ordinary sulphuric acid, sulphuric acid containing 5 per cent. of phenol or salicylic acid. A suitable quantity of the fertiliser together with a drop of mercury is placed in the flask, which is then held in cold water, preferably ice water. Phenolated or salicylated acid (previously chilled in ice, if available) is added suddenly, as has been already mentioned, and the flask, kept as cold as possible, is gently rotated for at least 10 minutes. Two g. of zinc dust (or 5 g. of sodium thiosulphate) is then slowly and cautiously added, still keeping the flask cool, then 10 g. of sodium or potassium sulphate. The mixture is heated very gradually and the process finally completed as already described.

It may happen, in view of the additional carbon contained in the phenol or salicyclic acid, that a further addition of sulphuric acid may be necessary during the process. The operator will judge from the appearance of the flask when this is necessary.

It is a matter of regret that this process, even with all the precautions indicated, is not infallible. If the compound fertiliser under investigation contains a large proportion of chlorides (as for example when potash may have been added in the form of "muriate" or of the low grade potash salts containing much sodium chloride as well as sodium or potassium nitrate), there is apt to be a small loss of nitric nitrogen—probably owing to the formation of compounds of nitrogen, oxygen and chlorine, before the NO_2 group is wholly fixed in the benzene ring. The writer has made some attempts to obviate or minimise this loss by the initial introduction of silver sulphate to fix the chlorine, not with invariable success, but with promising results. The matter is still under investigation. Unless the difficulty is finally overcome, it may possibly be necessary in exceptional cases to go back, to a modification of the old soda-lime process devised by J. Ruffle[1] in 1881. This modification consisted in the addition to the soda-lime of a liberal quantity of sodium thiosulphate, with sulphur and powdered charcoal. The process necessitated the use of a large iron combustion tube, and entails the close observance of precautions laid down by its author. It is hoped, however, that this reversion may, in the light of further investigation, prove to be unnecessary.

In certain fertilisers containing no nitrates, the "Kjeldahl-Gunning-Arnold" method also needs a small modification, viz., for calcium cyanamide or compound fertilisers of which that substance is a constituent. If concentrated sulphuric acid is used with calcium cyanamide itself, there is apt to be a small initial loss of nitrogen which in a sample containing 18 to 20 per cent. nitrogen may amount to as much as 0·5 per cent. This is obviated by first diluting 20 c.c. of sulphuric acid with 20 c.c. of water, and then proceeding as usual. Calcium cyanamide as a constituent of a mixed fertiliser is a further source of serious trouble if nitrates are also present in the mixture. In order to fix the nitric nitrogen, the acid should be concentrated; whereas for the purpose of dealing satisfactorily with the cyanamide nitrogen, it should, as already indicated, be diluted. The difficulty of dealing with mixtures of ammonium salts, calcium cyanamide and nitrates has been recognised in America, where a good deal of work has already been done in the attempt to arrive at a solution of the problem, but, thus far, not very successfully.

In the meantime, there is reason to suppose that the blenders of artificial fertilisers have become aware that if they mix calcium

[1] *J. Chem. Soc.*, 1881, **39**, 87.

cyanamide with nitrates they are liable, under the present regulations for official analyses, to lose credit for some of the nitrogen contained in their mixtures, and will therefore probably be led to modify their prescriptions accordingly.

Ruffle's dry combustion process in the hands of the writer has shown promise of utility for complicated mixtures of this kind, but it is tedious and its success depends upon meticulous observance of detail and nicety of manipulation calling for special experience and rigorous control by "blank" experiments with all the materials used.

Assuming the whole of the nitrogen to have been brought by appropriate treatment into the form of ammonium sulphate, its determination is then a matter of apparent simplicity. When the contents of the flask are cool, they are washed into a 1000 c.c. distillation flask (containing some fragments of granulated zinc to prevent bumping). As a result of the various quantities of wash-water, the volume of liquid in the flask will now be about 400 c.c. to 500 c.c. The flask is fitted with a doubly perforated indiarubber bung. In one aperture there is fixed a tapped funnel having a capacity of about 75 c.c. The nature or form of the delivery tube for the ammonia depends on the contrivance adopted for the reception or condensation of the distillate which in any case will be received in a measured quantity of standard sulphuric acid of convenient strength. The distillation can be carried out either with or without a condenser. In the latter case the steam must be allowed to bubble into the acid. If condensation is preferred, there are various forms of condensing apparatus which may be used, either single condensers or a large "box" condenser through which pass the delivery tubes from a number of distillations proceeding side by side.

As the distillation necessarily involves the use of an excess of sodium hydroxide, adequate precautions must be taken to avoid the passing forward of alkaline spray from the flask. Those not experienced in what appears to be so simple a matter as this distillation are often unaware of the extreme fineness of the spray generated in such a distillation or of the distance, even in a perpendicular direction, that such spray may be carried. Unless the exit tube rises to a considerable vertical height, the interposition of a bulb trap or "splash head" to intercept the spray is essential. (See any apparatus maker's catalogue.)

The writer has a strong preference for dispensing with the condenser, and for obviating difficulties due to "spray" still uses a very simple device which he adopted very early in the history of the Kjeldahl process and described in the paper[1] already alluded to (Fig. 84).

[1] *J. Chem. Soc.*, 1895, **67**, 811.

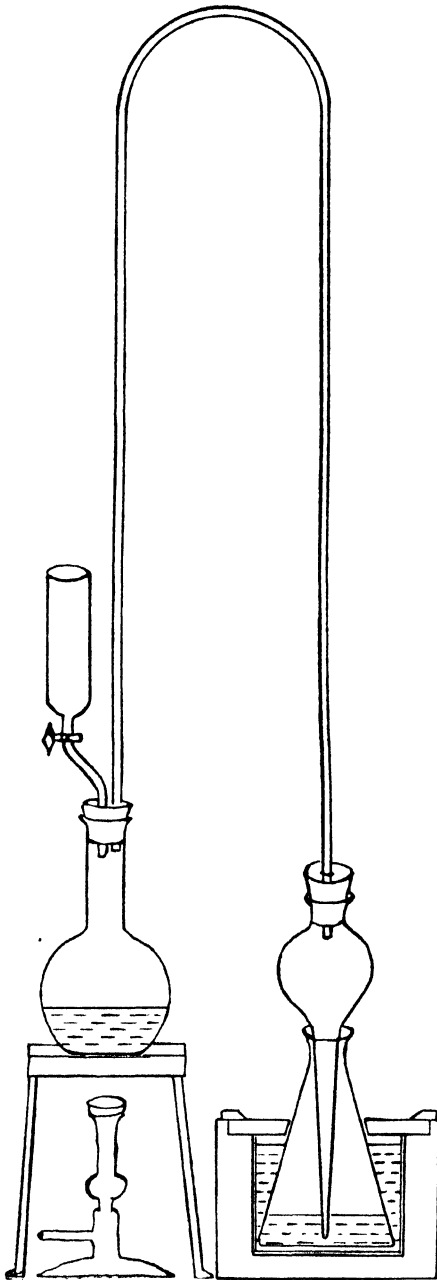



Fig. 84.

Into the outlet aperture of the distillation flask is fixed a block tin tube of $\frac{7}{16}$ inch external diameter and about $\frac{5}{16}$ inch internal diameter, having a length of $5\frac{1}{2}$ feet. This tube ascends vertically to a height of $2\frac{1}{2}$ feet above the bung of the flask and is then curved downwards, thus making a long inverted U-tube. The delivery end is fitted with another indiarubber bung which fits into a large pear-shaped bulb which dips (resting loosely in its mouth) into a 500 c.c. Erlenmeyer flask containing the measured quantity of standard acid into which the lower end of the bulb dips. Six or eight distillations are conducted side by side and the Erlenmeyer flasks are clamped by a suitable device side by side in a trough of running water.

The whole apparatus having been fixed in position, a quantity of concentrated sodium hydroxide solution—about 70 c.c. or sufficient to render the contents of the flask strongly alkaline—is introduced through the tapped funnel. If mercury has been used in the digestion process (it is invariably used by the writer), the operator will probably have noticed in washing out the flask an appreciable quantity of a yellow deposit which consists of mercury ammonium compounds. To ensure the decomposition of such compounds and so obviate loss of ammonia, it is necessary, when mercury has been used, to introduce, after the sodium hydroxide, 5 c.c. of a solution of 25 g. of sodium sulphide in 100 c.c. of water.

The contents of the flask having been mixed by a slight rotary movement, the contents of the flask are boiled briskly for not less than half an hour. The pear-shaped tube is then detached from the tin tube, and removed from the flask (being carefully "washed in" during the process) and the residual acidity of the liquid in the flask is titrated (preferably in a large porcelain basin) with methyl orange, methyl red, or cochineal as indicator. The writer prefers cochineal as being, to his eyes, more sharply sensitive.

It occasionally happens that there is a tendency to frothing during distillation. The careful introduction through the tapped funnel of a few c.c. of petroleum or paraffin oil will effectively check this inconvenience.

The possible presence of traces of nitrogen in the digestion acid, traces of alkali due to possible action of steam on the glass apparatus, error due to transition point in titration, etc., etc., must be compensated for by a "blank" experiment on a gram of pure sugar, and allowed for in the final titration. This "blank" should be repeated with every new bottle of sulphuric acid and every new batch of sodium hydrate solution. Under satisfactory conditions this error should not be more than about 0·2 c.c. of N/5 alkali.

The details of the distillation and collection of ammonia have been considered at some length, for during a long experience the writer has

often been appealed to for help or advice by operators who have been troubled by discordance in their results owing to what turned out to be insufficient realisation of sources of possible error in a process theoretically so simple.

The epitomised description of the foregoing methods for determination of nitrogen in fertilisers, either in absence or in presence of nitrates, given in the official directions of the Ministry of Agriculture,[1] being for local purposes binding in connection with any samples taken under the Act, is as follows :—

(iii) *Determination of Nitrogen.*

The presence or absence of nitrates shall first be ascertained :—

(a) *Nitrogen (organic and ammoniacal) in absence of nitrates.*

(A) A weighed portion of the sample shall be transferred to a Kjeldahl digestion flask, 25 millilitres of concentrated sulphuric acid (or more if necessary) shall be added and the flask gently heated until frothing ceases. Ten g. of potassium or sodium sulphate (anhydrous) shall then be added and the flask further heated until the colour of the clear liquid ceases to diminish. The digestion shall be continued for an hour thereafter to ensure complete oxidation of the organic matter. The operation may be accelerated by the addition of a small crystal of copper sulphate or a globule of mercury to the liquid in the digestion flask.

(B) The quantity of ammonia present in the liquid shall be determined by distillation into standard acid after liberation with alkali and, where mercury has been used, with the addition also of sodium or potassium sulphide solution.

(b) *Nitrogen (total, i.e., organic, ammoniacal and nitric) when nitrates are present.*

(A) A weighed portion of the sample shall be transferred to a Kjeldahl digestion flask; 30 millilitres of concentrated sulphuric acid, containing one g. of salicylic acid or one g. of phenol, shall be added and the flask shall be shaken so as to mix its contents without delay. The shaking shall be continued at intervals during ten minutes, the flask being kept cool, and then 10 g. of potassium or sodium sulphate (anhydrous) shall be added, together with either 5 g. of crystalline sodium thiosulphate or 2 g. of zinc dust. The flask shall be heated until the colour of the clear

[1] *Fertilisers and Feeding Stuffs Regulations*, 1928, issued 23rd May 1928. (Statutory Rules and Orders, 1928, No. 421.)

liquid ceases to diminish and for an hour thereafter. A further quantity of concentrated sulphuric acid may be added if necessary. Copper sulphate or mercury may be used as described in paragraph (iii) (a) (A).

B. Nitrogen Present as Ammonium Salts

Among fertilisers in which the nitrogen is already combined as ammonia or ammonium salts, the simplest is ammonium sulphate, but a vendor sometimes indicates that a certain proportion of the nitrogen content in a compound fertiliser shall be in the form of ammonium salts. In the examination of ammonium sulphate, all that is necessary is to introduce any convenient quantity, say 1 to 1·2 g., into the distilling flask, add a sufficient quantity of water and an excess of sodium hydroxide and distil as already described.

In fertilisers containing an admixture of organic matter, the use of sodium hydroxide may result in an over-estimate of the nitrogen originally present as ammonium salts due to the formation of ammonia from organic nitrogenous matter. To meet this difficulty, magnesium oxide is used to liberate the ammonia. The official directions of the Ministry of Agriculture (May 1928) are as follows :—

Nitrogen in form of Ammonium Salts.

(*Note*: In the case of compound fertilisers containing calcium carbonate with small quantities of ammonium salts, the portion taken for analysis must be dissolved in hydrochloric acid and the solution used for distillation with alkali.)

(1) *In absence of organic matter.* A weighed portion of the sample shall be dissolved in water and made up to a definite bulk. An aliquot part of the solution shall be transferred to a distillation flask and the quantity of ammonia shall be determined as above prescribed in paragraph (B).

(2) *In presence of organic matter.* A weighed portion of the sample shall be transferred to a distillation flask with about 200 millilitres of water and 5 g. of magnesium oxide, free from carbonates, and the quantity of ammonia determined by distillation into standard acid.

Unfortunately, however, the familiar commercial calcium cyanamide made for agricultural use, which contains nitrogen in various forms of combination, sometimes including urea, yields appreciable quantities of ammonia in alkaline distillation even with magnesia; so that if calcium cyanamide is present in a compound fertiliser the production of ammonia on distillation from magnesia is not necessarily evidence of the presence of ammonium salts in the original mixture.

C. Nitrogen as Nitrates

The determination of nitrogen in the form of nitrates, as apart from total nitrogen, is sometimes necessary in the examination of compound fertilisers and is constantly required in the examination of commercial sodium and potassium nitrates.

It is proposed here to deal with only three methods, viz., the methods of Devarda[1] and of Ulsch (both of which are well known and now official in England; *cf.* Vol. I., p. 474) and another, viz., the Indigo method, which is less well known.

Devarda's Method.—This method is based on the conversion of nitric nitrogen into ammonia by the action of potassium or sodium hydroxide on a powdered alloy of aluminium, copper and zinc, familiarly known as and purchasable under the name of "Devarda Metal" or "Devarda's Alloy." The details of the process are succinctly given in the directions of the Ministry of Agriculture quoted below.

Ulsch's Method. (*Cf.* Vol. I., p. 476).—The officially alternative Ulsch method depends upon the reduction of nitrate to ammonium sulphate when the nitrate solution is warmed with dilute sulphuric acid in presence of reduced iron. Sufficient directions for this process are also given in the following regulations of the Ministry. The writer has a preference for the Devarda method over that of the Ulsch, and believes that this preference is generally shared by those having experience of both methods. A weak point of the Ulsch process is that reduced iron commonly contains quantities of nitrogen which are usually large enough to necessitate a rather large correction from the "control" or "blank" experiment; and there is no certainty that the quantity of nitrogen in the 10 g. of reduced iron used in the analysis is the same as that in the 10 g. used for "control"; nor is it certain that small and unintentional variations in the mode of conducting the experiment may not affect the quantity of ammonia yielded by nitrogen present as impurity in the iron even if it is assumed to be evenly distributed. In the Devarda process the correction necessitated on the basis of the "blank" or "control" experiment is, in the writer's experience, with the reagents at present obtainable, much smaller.

The official regulations of the Ministry of Agriculture are as follows :—

(d) *Nitrogen in Nitrates.*[2]

(1) *In absence of organic matter.*

(A) A weighed portion of the sample shall be dissolved in water and made up to a definite bulk. An aliquot part of

[1] *Landw. Versuchs-Stat.*, 1893, **42**, 130.

[2] *Fertilisers and Feeding Stuffs Regulations*, Ministry of Agriculture, 1928.

the solution shall be transferred to a flask and a quantity of finely powdered Devarda metal added. The quantity of Devarda metal shall be not less than six times the weight of the sample present in the aliquot part taken. An excess of concentrated alkali shall then be added and the flask at once connected with a distillation apparatus. After standing for thirty minutes to allow the reaction to proceed, heating gently if necessary, the ammonia shall be distilled over into standard acid.

(B) *Alternative method.* Ten g. of the sample shall be dissolved in water and the solution made up to 500 millilitres. Fifty millilitres of the solution shall be placed in a half-litre Erlenmeyer flask and 10 g. of reduced iron and 20 millilitres of sulphuric acid of 1·35 sp. gr. shall be added. The flask shall be closed with a rubber stopper provided with a thistle tube, the head of which shall be half filled with glass beads, and allowed to stand until effervescence ceases. The liquid shall then be boiled for five minutes, the flask removed from the flame and any liquid that may have accumulated among the beads rinsed back with water into the flask. The solution shall be boiled for three minutes more and the beads again washed with a little water. The quantity of ammonia shall then be determined as described in paragraph (B). (See total nitrogen, p. 503.)

(2) *In presence of organic matter.*

One g. of the sample shall be placed in a half-litre Erlenmeyer flask with 50 millilitres of water. Ten g. of reduced iron and 20 millilitres of sulphuric acid of 1·35 sp. gr. shall be added and the procedure prescribed in paragraph (iii) (d) (1) (B) above shall be followed, except that the quantity of ammonia contained in the liquid, after the treatment with reduced iron, shall be determined by distillation after addition of magnesium oxide as in paragraph (iii) (c) (2). In cases in which the proportion of nitrates is small, a larger quantity of the sample shall be taken.

The regulations also contain the following useful caution:—

(e) *Control Experiment in Determination of Nitrogen.* The materials used in any of the methods described in paragraph (iii) shall be examined as to their freedom from nitrogen by means of a control experiment carried out under similar conditions with the same quantities of the reagents which have been employed in the actual analysis in the case of (a), one g. of pure sugar being used in place of the weighed portion of the

sample. The quantity of standard acid found to have been neutralised in the control experiments shall be deducted from the total quantity of acid neutralised in the distillation of the sample.

Neither the Devarda process nor the Ulsch process is reliable for the determination of nitrates in mixed fertilisers containing calcium cyanamide. If an aqueous solution of commercial calcium cyanamide is subjected to the treatment prescribed for the Devarda process, 80 to 90 per cent. of its nitrogen is yielded in the form of ammonia; and from what has been already said as to the formation of ammonia in the distillation of cyanamide in presence of alkali, it follows that even the Ulsch process will yield no accurate results for nitrate in the presence of this substance.

The Indigo method about to be described, also breaks down altogether in a solution containing calcium cyanamide, although, as may be anticipated, the latter has no decolorising effect on indigo. On the other hand, it has such a strong reducing action on nitrates when sulphuric acid is added to the solution that the results by the Indigo method are meaningless in presence of calcium cyanamide.

Indigo Method.—The Indigo process was due to Boussingault and was in constant use for water analysis in the early "seventies," and at that time the process was subjected by Warington[1] to critical investigation at Rothamsted in connection with its use for the analysis of soil drainage water. For many purposes the process yields accurate results in the hands of a skilful operator. It is still in everyday use in the laboratory of the writer and in a few other laboratories (*cf.* p. 455).

It depends upon the decoloration of indigo solution by nitric acid when a solution of nitrates is mixed with an equal volume of concentrated sulphuric acid. The indigo solution is made by dissolving 5 g. of pure indigo-carmine in 200 c.c. of concentrated sulphuric acid. Of this solution 100 c.c. is diluted with distilled water to 2000 c.c. when 1 c.c. will correspond to about 0·0001 g. of N_2O_5, but must be accurately standardised by means of a dilute standard solution of potassium nitrate corresponding to 0·001 g. N_2O_5 per c.c. Three c.c. of this solution, measured with very close accuracy (being equivalent to 0·003 g. of N_2O_5) is diluted in 20 c.c. distilled water in a beaker and about 25 c.c. of the indigo solution run in from a burette. Fifty c.c. of strong sulphuric acid is quickly poured into the beaker, with vigorous stirring, more indigo solution being rapidly added from the burette until the blue colour persists. In this first trial some of the nitric acid will have been lost by evolution before it has had time to attack the indigo. The experiment is then repeated, adding to the

[1] *Chem. News*, 1877, 35, 45, 57; *J. Chem. Soc.*, 1877, 32, 735; also 1879, 35, 578.

nitrate solution more of the indigo than was consumed in the first trial, but doing so *before* the addition of sulphuric acid. After addition of the latter, more indigo is rapidly added, as before, until the solution remains blue. The experiment is again repeated on similar lines until the final addition of indigo solution required for permanent blue colour is reduced to about ½ c.c. By this "trial and error" method, an experienced operator can standardise indigo to the necessary degree of accuracy in about a quarter of an hour.

A dilute solution of the material to be tested is preliminarily examined in order to ascertain approximately how much of it will decolorise, say, 30 c.c. of the standard indigo solution. When the approximate quantity of indigo solution required has been ascertained, such quantity is mixed with the nitrate solution, diluted with water to 50 c.c., an equal volume of sulphuric acid rapidly added as before, further indigo being then run in as already described. The experiment is repeated until a close end-point is hit.

In the experience of the writer, no extraneous heat need be applied to the contents of the beaker, provided that the sulphuric acid used is of the strength of "pure" sulphuric acid as ordinarily supplied for laboratory use, as the temperature generated by this admixture with the aqueous solution will be sufficiently high. If the acid is weak, the final decoloration of the indigo is delayed and the result is indeterminate. Needless to say, the acid must be free from any impurity capable of decolorising indigo under the conditions of the experiment.

As success largely depends upon the skill and experience of the operator, it is obviously not a process which could be laid down as an "officially prescribed" method for general use.

D. Nitrogen Soluble in Permanganate (*Street*)

The Official Methods of Analysis of the Association of Official Agricultural Chemists of America include two methods for distinguishing between organic nitrogenous matter attacked or rendered soluble by potassium permanganate, and nitrogen not so attacked, the object being to make some discrimination between nitrogen likely to become available for plant food within a reasonable time after it is added to the soil and nitrogen that may be regarded as comparatively unavailable. This attempted method of differentiation was originally introduced by Street of Connecticut as the result of comparative experiments on a number of organic fertilisers known from actual cultural experience to differ in their fertilising effect either in their ultimate realisable value or in their speed of action.

It is open to question how far a comparison between the drastic action of a substance like permanganate on the one hand and the rate

of decay and consequent ammonification and nitration under the biological influences at work in any given soil, is to be regarded as practically valid; but in America it has long been accepted that the results thus empirically obtained in the laboratory afford some approximate indication of comparative "availability," although during 1928 the "Committee on Fertilisers" of the American Association issued the following note disclamatory of too narrow an interpretation of the results:—

"The alkaline and neutral permanganate methods distinguish between the better and the poorer water-insoluble nitrogen, and do not show the percentage availability of the material. The available nitrogen of any produce can be measured only in carefully conducted vegetation experiments."

Nevertheless, as the permanganate process remains official in America, and as its results are regularly taken into account there in the valuation of organic fertilisers, analysts in this country are frequently called upon to determine what is usually shortly referred to in commerce as "Street availability," or "Availability by the Street process," in organic fertilising materials intended for export to America. It is therefore recorded here.

There are two alternative methods, one called (not quite correctly) the "Neutral Permanganate Method" and the other the "Alkaline Permanganate Method."

Neutral Permanganate Method.—In this method the differentiation is between organic nitrogen dissolved by a solution of potassium permanganate and sodium carbonate, and the organic nitrogen not so dissolved. As the process is purely empirical and the results depend upon the exact observation of the conditions laid down, it is here given in full from the "Methods of Analysis" of the Association of Official Agricultural Chemists (Washington, D.C.), second edition, revised to 1st July 1924, published in 1925.

Water-Insoluble Organic Nitrogen Soluble in Neutral Permanganate: Preliminary Test (Determination of Water-Insoluble Organic Nitrogen).

Place 1 or 1·4 g. of the material on an 11 cm. filter paper and wash with water at room temperature until the filtrate measures 250 c.c. Dry and determine nitrogen in the residue . . . making a correction for the nitrogen of the filter, if necessary.

Place the quantity of fertiliser equivalent to 50 mg. of water-insoluble organic nitrogen, as determined (above), on a moistened 11 cm. filter paper and wash with water at room temperature until the filtrate measures 250 c.c. Transfer the insoluble residue with 25 c.c. of tepid water to a 400 c.c. Griffin low-form beaker, add 1 g. of

sodium carbonate, mix, and add 100 c.c. of a 2 per cent. potassium permanganate solution. Cover with a watch-glass and immerse for thirty minutes in a steam-bath or in a hot-water bath so that the level of the liquid in the beaker is below that of the water in the bath. Stir twice at intervals of ten minutes. At the end of thirty minutes, remove from the bath, add immediately 100 c.c. of cold water, and filter through a heavy 15 cm. folded filter. Wash with small quantities of cold water until the filtrate measures about 400 c.c. Determine nitrogen in the residue and filter . . . correcting for the nitrogen, contained in the filter. The nitrogen thus obtained is the inactive water-insoluble organic nitrogen. To obtain the water-insoluble organic nitrogen soluble in neutral permanganate, subtract the percentage of nitrogen from that obtained (above).

For the alternative variation of the process the initial procedure is similar. The nitrogenous matter broken down by the permanganate is estimated by its conversion into ammonia much as in the "albuminoid nitrogen" process of Wanklyn, still in use for water analysis (see p. 417).

The directions for this process have been modified as follows.[1]

Alkaline Permanganate Method.—Dry the residue remaining after treatment of the material as already described (viz., washing out with water) at a temperature not exceeding 80° and transfer from the filter to a 500 to 600 c.c. Kjeldahl distillation flask, loosening adhering particles by rubbing gently with a stiff brush, but avoiding the transfer of portions of the brush or of paper fibres. Add 20 c.c. of water, fifteen to twenty small glass beads or fragments of pumice stone, a drop of mineral lubricating oil weighing not more than 50 mg., and 100 c.c. of alkaline permanganate solution. Connect with an upright condenser to the lower end of which has been attached a 100 c.c. graduated cylinder containing standard acid and so arranged as to receive the distillate below the surface of the acid or otherwise so trapped as to prevent loss of ammonia. Digest slowly with a very low flame for thirty minutes, barely below distillation point, using coarse wire gauze and asbestos paper between the flask and flame. Gradually raise the temperature and, after all danger from frothing has passed, distil 95 c.c. in sixty minutes (plus or minus five minutes), controlling the distillation so that approximately 24 c.c. of distillate is obtained in each fifteen-minute period. Conduct the first part of the distillation over a bare flame but use wire gauze ten minutes before completion to avoid breaking the flask. Transfer the distillate to an Erlenmeyer flask or to a beaker and titrate with standard alkali, using cochineal or methyl red indicator. When a tendency to froth is noticed, lengthen the digestion period, and no trouble will be experienced

[1] *J. Assoc. Off. Agric. Chem.*, 1928, 11, 34.

when the distillation is begun. During the digestion gently rotate the flask occasionally, particularly if the material shows a tendency to adhere to the sides.

The nitrogen thus obtained is the active water-insoluble organic nitrogen.

Whichever of the permanganate processes is used, it is prescribed that the samples shall be preliminarily ground so as to pass a sieve having circular openings of 1 mm. in diameter. This prescription limits the coarseness of the coarsest particles to be operated upon, but obviously puts no limitation upon the fineness of the finer particles, which must depend upon the mode of grinding; but it serves as a caution against the deliberate reduction of the sample to fine powder. There shall be no more grinding of the material beyond that necessary to ensure complete passage through the prescribed sieve. The more finely ground the material is, the more of the organic matter is likely to be attacked by the permanganate, especially in the so-called "Neutral" process. The method is intended to apply to the effect of permanganate on the material in as nearly as possible the physical or mechanical condition in which it would be used as a fertiliser.

It is the former of the two methods, the so-called "Neutral Street Permanganate Method," that is commonly in request for commercial analyses and the results are usually returned thus:

	Per cent.
Total Nitrogen	——
Equal to Ammonia	——
Including:—	
Nitrogen dissolved by permanganate solution working by the American Official Street method . . .	——
Equal to Ammonia	——

The nitrogen dissolved by permanganate being the difference between the nitrogen not so dissolved and the total nitrogen, being inclusive therefore of whatever initially water-soluble nitrogen there may be present.

A fuller statement may sometimes be required differentiating between water-soluble nitrogen, water-insoluble nitrogen dissolved by permanganate, and water-insoluble nitrogen not so dissolved.

CALCIUM CYANAMIDE

Total Nitrogen.—Attention has been already drawn (see p. 499) to the necessity of a small departure from the usual or official form of the Kjeldahl-Gunning-Arnold method, viz.:—the dilution of the concentrated sulphuric acid with 20 c.c. of water before pouring it on to the cyanamide, there being, unless this precaution is taken, an appreciable loss of nitrogen. This modification is recognised in

the methods in use in Germany, but has not been taken into account in drawing up the present official English methods.

Dicyandiamide is apt to be present in calcium cyanamide especially if the material has been for a long time in storage or has become damp. Its presence is undesirable for various reasons and the analyst is therefore sometimes called upon to distinguish between nitrogen present in this form and that present in other forms, which it may be observed include not only calcium cyanamide but also sometimes urea and a number of related compounds. Nitrogen present as dicyandiamide may be determined by taking advantage of the insolubility of silver cyanamide in presence of excess of ammonia and the solubility under like conditions of the silver salt of dicyandiamide, the latter, however, being precipitable from such solution by sodium hydroxide.

Various methods have been described. A. Stutzer[1] proceeds as follows:—10 g. of the calcium cyanamide sample is shaken up with 100 c.c. of 94 per cent. alcohol for two hours. The alcohol extracts the dicyandiamide and some other bodies, if present (*e.g.* urea), but leaves the great bulk (though not quite all) of the calcium cyanamide undissolved. The alcoholic solution is filtered and 50 c.c. of the filtrate is diluted with 180 c.c. of water followed by 10 c.c. each of 10 per cent. silver nitrate solution and 10 per cent. solution of ammonia. A slight precipitate will be formed representing the small quantity of calcium cyanamide dissolved by the alcohol. This precipitate is filtered off. Of the undiluted filtrate 200 c.c. is taken, representing 4 g. of the original sample. To this solution 50 c.c. of 10 per cent. solution of sodium hydroxide is added, without heating, when the dicyandiamide is precipitated as silver salt. This is filtered off and washed with cold water, and the nitrogen determined in it by the Kjeldahl method as already described for total nitrogen. The nitrogen found is the nitrogen present as dicyandiamide, and multiplied by 1·5 gives the percentage of that compound $(CN.NH_2)_2$.

The method has been later modified by Hager and Kern,[2] who proceed, like Stutzer, by shaking up 10 g. of the sample with 100 c.c. of 94 per cent. alcohol. The solution is filtered and two separate portions of 40 c.c. each are taken, each being diluted with 150 c.c. of water. In one portion the small quantity of calcium cyanamide dissolved by the alcohol is precipitated with silver nitrate and ammonia, the aggregation and separation of the precipitate being expedited by the addition to the solution of a few drops of sodium phosphate solution. The precipitate is filtered off and washed and the nitrogen therein determined. In the other portion of diluted alcoholic filtrate, the cyanamide and dicyandiamide are precipitated

[1] *Z. angew. Chem.*, 1916, 29, 417-8. [2] *Z. angew. Chem.*, 1917, 30, 53.

together with silver nitrate solution, making the solution slightly but distinctly alkaline with sodium hydroxide and using phenolphthalein as indicator. After brisk stirring, the precipitate is filtered off and the nitrogen therein determined, the difference between the nitrogen in the two precipitates representing that present as dicyandiamide.

Calcium Carbide.—Small quantities of calcium carbide are sometimes present in calcium cyanamide and a limitation of this quantity, sometimes fixed as low as 0·1 per cent., is sometimes indicated in contracts. The carbide is determined in 5 g. of the sample, well mixed with a few grams of recently ignited sand. This mixture is placed in a small "oil flask" having a volume of not more than 100 c.c. into which is introduced (of course without spilling) a short wide test tube containing 10 to 12 c.c. of cold boiled distilled water. The flask is closed with an india-rubber stopper bearing a bent outlet tube which is closely connected by an india-rubber joint with a nitrometer filled with brine. The tube in the flask is then upset and thoroughly mixed with the solid contents of the flask by gentle shaking and a vessel of hot water is then cautiously and intermittently, and finally continuously, applied to the flask until no further expansion of gas is indicated, the nitrometer being handled in the usual way. Finally the whole is allowed to cool, the pressure in the two limbs of the nitrometer equalised, and the volume of gas read off in the usual way and corrected for temperature and pressure. The volume of gas at N.T.P. is taken as acetylene and the calcium carbide calculated therefrom. It has been suggested that the water in the small tube in the flask should be first saturated with acetylene. This would be reasonable if the operation were entirely conducted in the "cold," but unless heat is applied, the last traces of calcium carbide appear not to be decomposed, and if heat is applied, acetylene with which the water may have been preliminarily saturated will be evolved.

The writer, who has had some experience of the method, has arrived at the conclusion that more accurate and consistent results are obtained by using non-acetylenated water and relying upon heat for the expulsion of the acetylene formed from the carbide.

Determination of Free Acid in Sulphate of Ammonia

It is frequently necessary to determine the free acid in sulphate of ammonia, importance being attached to very minute quantities of acid, should any be present, in those grades of sulphate of ammonia which are commercially described as "neutral." The determination is necessarily empirical, as the estimation of free acid depends upon the behaviour of the solution towards an indicator and, as is very well known, different indicators give different points of assumed

"neutrality" in the same solution. In the case of sulphate of ammonia, for example, methyl orange and methyl red will give different neutrality points in the same solution of a slightly acid ammonium sulphate. For commercial purposes it has therefore been necessary to prescribe conventionally the indicator which is to be used. The sulphate of ammonia industry has pressed the use of *methyl orange* as indicator and this has now been officially adopted. The method is given in the following regulations of the Ministry of Agriculture, 1928.

> (vi) *Determination of Free Acid in Sulphate of Ammonia.*—Twenty g. of the sample shall be dissolved in about 50 millilitres of neutral distilled water and the solution filtered. The filtrate shall be made up to about 250 millilitres and then titrated with decinormal sodium hydroxide solution, using two or three drops of methyl orange solution as indicator. The methyl orange solution shall contain 0·5 g. of methyl orange in a litre of water. The result shall be expressed as percentage by weight of sulphuric acid (H_2SO_4).

II.—PHOSPHORIC ACID

In phosphatic fertilisers or in the raw materials from which they are manufactured, the analyst may be called upon to determine merely total phosphoric acid or to differentiate between total phosphoric acid and phosphoric acid soluble in water, or between total phosphoric acid and phosphoric acid dissolved by some more or less arbitrarily prescribed solvent designed to afford some measure of relative "availability" as plant food, such as dilute citric acid or ammonium citrate, either alkaline or neutral.

Two points to be considered in the determination of phosphoric acid are, first, the method by which the phosphoric acid is to be brought into solution; and secondly, its determination when so dissolved.

The former question must be considered in relation to the particular material under examination, and it will be convenient to consider first the determination of phosphoric acid in mineral phosphate, which forms the manufacturing raw material of superphosphate and of the numerous compound fertilisers into whose composition superphosphate enters.

1. PHOSPHORIC ACID IN RAW MINERAL PHOSPHATES

Three methods are in use for the commercial analysis of mineral phosphates, viz., the molybdate method in one of its many variations, the direct citric-ammonium-magnesium method and the more complicated but more exact citric-oxalic-ammonium-magnesium method.

The first and third, if properly carried out, are of a high degree of accuracy and yield identical results. The second method is rapid but only approximate, and some raw phosphates give high results.

Molybdate Process.

This process is based upon the separation of phosphoric acid in the form of ammonium phosphomolybdate and the subsequent solution of the precipitate in ammonium hydroxide and reprecipitation of the phosphoric acid as ammonium magnesium phosphate and conversion of the latter by ignition into magnesium pyrophosphate. This process has been the subject of almost ceaseless investigation since it was originally devised by Sonneschein in 1851, and an enormous number of modifications have been introduced or suggested. Recent American chemical literature is rich in records of "team work" on the subject. It was only gradually that it became evident that the discrepancies of varying magnitude so often observed have been mainly due to the fact that the ammonium magnesium phosphate precipitated from the ammonia solution of the molybdate precipitate has not necessarily the simple constitution assigned to it, but may be to some degree a mixture or complex of phosphates in which the proportion of magnesium to ammonium may vary to an extent which may appreciably affect the ultimate weight of the ignited residue, usually assumed to be wholly magnesium pyrophosphate. Much work has therefore recently been done in observing the ultimate variations brought about by the neutralisation in a varying degree of the ammoniacal solution prior to the addition of magnesia mixture, as well as in the observation of the effect of variations in temperature at the time of precipitation.

It is now unnecessary to give a detailed discussion of the matter in view of the able summary of the whole subject by G. Jörgensen[1] of Christiania, who has worked continuously on the subject for at least thirty years. This embodies his own final modification of the process, which may be accepted as affording the nearest approach to scientific accuracy.

Jörgensen's Modification of the Molybdate Method. *Preparation of the Reagents.* (a) *Molybdate Solution.*—One hundred g. of pure ammonium molybdate is dissolved in 280 c.c. of ammonia (sp. gr. 0·97) and 300 c.c. of this solution is poured, with vigorous shaking, into 700 c.c. of nitric acid (sp. gr. 1·21), and the mixture allowed to stand for twenty-four hours. The ammonia solution may be prepared by mixing 84 c.c. of ammonia (sp. gr. 0·91) with 196 c.c. of water, and the

[1] "The Determination of Phosphoric Acid as Magnesium Ammonium Phosphate," G. Jörgensen, *Analyst*, 1926, 51, 61.

nitric acid by mixing the strong acid (sp. gr. 1·4) with about an equal weight of water.

(b) *Acid Ammonium Nitrate Solution.* This should contain 40 g. of ammonium nitrate and 10 g. of nitric acid per litre. It is prepared by mixing 90 c.c. of nitric acid (sp. gr. 1·4) with about 1500 c.c. of water, adding 80 c.c. of ammonia (sp. gr. 0·91), and making up to a volume of 2000 c.c.

(c) *Magnesia Mixture.* Fifty g. of pure crystallised magnesium chloride ($MgCl_2.6H_2O$) and 150 g. of pure ammonium chloride are dissolved in water and the solution made up to a litre.

Method for Mineral Phosphates. Five g. of mineral phosphate is placed in a 250 c.c. flask and gently boiled for about half an hour with 25 c.c. of nitric acid (sp. gr. 1·21) and 12·5 c.c. of hydrochloric acid (sp. gr. 1·12). The contents of the flask are then cooled, made up to 250 c.c., and filtered.

To 50 c.c. of the filtrate contained in a beaker flask (250 c.c.) is added the quantity of molybdic solution shown in the equation—

$$x = 0.12\,v + 345\,p$$

where x = c.c. molybdate solution, v = c.c. of the phosphate solution, and p = g. of P_2O_5 (expected), the flask placed in a water-bath at a temperature of 50° for ten minutes, and its contents occasionally stirred. It is allowed to cool and when quite cold (*e.g.* after immersing the beaker flask in cold water for fifteen minutes) the contents are filtered, and the precipitate washed ten times by decantation with acid ammonium nitrate solution, about 20 c.c. being used for each washing. If necessary, the filtrate may be tested for unprecipitated phosphate by adding more molybdic solution, heating to 50°, and leaving for twelve hours. The detection of calcium, as a test of the washing being sufficient, may be made by adding a little sulphuric acid and alcohol to the extent of twice the volume of the washings.

The washed molybdic precipitate is dissolved in 100 c.c. of 2·5 per cent. ammonia solution, filtered, if necessary, through the filter which held the molybdic precipitate, the filter being washed eight times with about 10 c.c. (each time) of the ammonia solution, so that the final volume is about 180 c.c.

The beaker flask is covered with a clock-glass, the contents brought just to the boiling-point, the flask removed from the burner, and 30 to 35 c.c. of the magnesia solution added, drop by drop, from a burette with a glass cock, the whole being well stirred. The beaker flask is again covered, and so long as the liquid remains very warm it is stirred frequently, and if the precipitate is not compact and crystalline the stirring should be continued. After standing for at least four hours the solution is filtered through a platinum crucible packed with spongy

platinum, and the precipitate washed with 2·5 per cent. ammonia solution until free from chlorides, and then once with alcohol.

The precipitate is dried and heated gradually over an Argand burner, then ignited strongly, cooled, and weighed. If all the above precautions are fully observed, the weight of magnesium pyrophosphate thus obtained accurately represents the phosphoric acid present.

The present writer makes one modification when applying Jörgensen's process. He prefers to use an accurately weighed quantity of about 1 g. of the finely ground phosphate, dissolving in hydrochloric acid, evaporating to dryness, moistening again with a little hydrochloric acid, taking up with nitric acid and water, filtering, thoroughly washing the precipitated silica and using the whole of the filtrate (after concentration on a water-bath) for the phosphoric acid determination. This is alternative to Jörgensen's method of taking 5 g., making up to bulk and taking an aliquot part of the solution representing 1 g. of the phosphate. The object of this modification (apart from making certain of the absence of soluble silica) is to avoid any error that may occur incidental to the use of a pipette. The accurate use of even a properly calibrated pipette demands the exercise of close and conscientious attention, any relaxation of which may tell appreciably when dealing with a material containing probably upwards of 70 per cent. of tricalcium phosphate, in the analysis of which the results obtained in a laboratory of recognised responsibility are expected to vary by not more than ±0·05 per cent. of phosphoric anhydride.

Ullmann, at the International Congress of Applied Chemistry held in London in 1907, described a modification of the molybdic process in which the direction was given to add the magnesia mixture to the ammoniacal solution of the phosphomolybdic precipitate at a temperature from 60° to 80°, and this method has been, for many years, adopted in Germany. This was a recognition of the desirability of a higher temperature than was previously in common use, but fell short in safety of Jörgensen's bolder advance of throwing down the precipitate from a boiling solution, as already described.

The directions given for the molybdic process in the *American Official Methods of Analysis*, in 1924, state that the ammoniacal solution of the phosphomolybdic precipitate is to be "nearly neutralised with strong hydrochloric acid" before addition of magnesia mixture. These directions have recently been modified,[1] "nearly neutralise" being replaced by the direction to "neutralise with strong hydrochloric acid, using litmus paper or bromothymol blue as an indicator." There is, however, no instruction as to the temperature at which the magnesia mixture is to be added.

[1] *J. Assoc. Off. Agric. Chem.*, 1929, **12**, 33.

The volumetric application of the molybdate method is discussed on p. 536.

Citric-Oxalic-Magnesium Method

This method, when properly carried out, is a reliable alternative to the molybdate method.

This method is based upon the effect of citric acid in retaining in solution iron and aluminium compounds, while from such a solution, if first neutralised and then rendered acid with acetic acid, calcium may be quantitatively precipitated as oxalate, the phosphoric acid being subsequently precipitated as ammonium magnesium phosphate. The method was in extensive use sixty years ago, but was uncertain in its results owing to contamination of the ammonium magnesium phosphate with magnesium oxalate, this error varying with the excess of oxalate used in precipitating the calcium, and upon various other conditions. Owing to this difficulty the process was avoided or abandoned by many early workers. It was found, however, that if, after the precipitation of ammonium magnesium phosphate, the bulk of the liquid was removed by filtration and the ammonium magnesium phosphate redissolved in hydrochloric acid and reprecipitated, this source of error was largely avoided. The process in this improved form was in use in the laboratory of the late Dr A. Voelcker, Consulting Chemist to the Royal Agricultural Society, in 1870 or earlier, and also in other agricultural laboratories where the result of Dr Voelcker's experience was known. The process as then used was, however, subject to minor inaccuracies from various sources; but these were gradually detected or obviated, and the method has since been in regular use in this country in laboratories in which commercial analyses of phosphate are carried out.

The knowledge of the process for the most part depended upon personal communication or traditional information and, so far as the writer is aware, although given in abbreviated form in some text books,[1] it had not been described with all the details requisite for strict accuracy until set forth by the present writer,[2] in 1912. Substantially the same account of the process appears in the current (3rd) edition,[3] from which the following is quoted by permission of the publishers. The details appear complicated, but in practice the process is simple and easy, if a little tedious, and if the precautions set forth are faithfully observed, the results are identical with those obtainable in the accurate working of the molybdate process as recommended by Jörgensen.

[1] *Cf.* Church's *Laboratory Guide*, revised by Kinch, 9th ed., 1912.
[2] *Thorpe's Dict. of Applied Chemistry*, 2nd ed., 1912.
[3] *Ibid.*, 3rd ed., 1922, 8, 185.

Two g. of the mineral phosphate is treated with not less than 25 c.c. of strong hydrochloric acid in a beaker covered with a clock-glass to avoid loss by spraying. After a few minutes' warming, the clock-glass is washed down into the beaker and removed, the beaker being placed in a water-bath and the contents evaporated to dryness. This results in the elimination from solution not only of silica but of fluorine compounds, the removal of which is essential to the accuracy of the process. Mere evaporation to dryness with a small quantity of hydrochloric acid is insufficient to ensure this removal, and it is necessary to use at least the large quantity of acid specified (25 c.c.), so that its evaporation may extend over several hours. (The non-observance of this precaution is a fruitful source of error, resulting in the subsequent formation of magnesium fluosilicate and consequent over-estimation of phosphoric acid.) The dry residue is taken up with 5 or 10 c.c. of hydrochloric acid and about 20 c.c. of water, and warmed. The silica, together with pyrites or other insoluble matter, is filtered off and thoroughly washed. To the filtrate and washings (measuring about 150 c.c.) 4 g. of powdered citric acid is added and 3 to 4 g. of powdered ammonium oxalate. The solution is heated nearly to boiling, and rendered just alkaline with dilute ammonia (sp. gr. about 0·970), excess of acetic acid is immediately added and the liquid is boiled for a few moments. The calcium oxalate is immediately filtered off and washed several times with boiling water, dried, ignited over a yellow Argand flame, and weighed as calcium carbonate. The precipitate contains all the calcium. It may contain minute quantities of ferric oxide, aluminium oxide, or manganese oxide, and a minute quantity of phosphoric acid. On this account the precipitate, after being weighed, is dissolved in dilute hydrochloric acid, the solution being boiled and treated with a slight excess of recently diluted ammonia. The small precipitate which forms is filtered through a small filter, washed, and redissolved in a little dilute acid, the solution boiled and again treated with a slight excess of ammonia. The precipitate is rapidly filtered and washed, ignited, and weighed. If this small precipitate weighs only 5 or 6 mg. or less (as is usually the case in the hands of a practised worker), it may be assumed that the precipitate contains P_2O_5 equal to half its own weight of $Mg_2P_2O_7$, this assumption being based on the analysis of a large number of such precipitates. But if, owing to unskilful work or to any peculiarity in the mineral under investigation, the quantity is greater, the small precipitate may be redissolved in hydrochloric acid, with the addition of about 0·1 g. of citric acid and its solution added to the original filtrate from the calcium oxalate precipitate.

This filtrate is made strongly ammoniacal and the phosphoric acid precipitated by the gradual addition of magnesia mixture, a large

excess being finally added. Gradual addition and vigorous stirring are both necessary to ensure that the precipitate comes down in a compact crystalline form. The whole bulk at this stage will be about 350 c.c. After two to three hours, during which the liquid is frequently stirred—or better, after standing over night—the greater part of the liquid is decanted off through a close filter, leaving about 40 c.c. in the beaker with the precipitate. The filter is washed with dilute hydrochloric acid, the washings being used to redissolve the precipitate in the beaker. After complete re-solution, the contents of the beaker are rendered ammoniacal by slowly dropping in dilute ammonia with vigorous stirring until the precipitate assumes as before a dense crystalline form. Excess of ammonia solution (sp. gr. 0·880) equal to about one-fifth or one-sixth of the bulk of the liquid is added and the whole allowed to stand with occasional vigorous stirring for at least one hour (preferably two hours). The precipitate is then filtered, washed well with ammonia (sp. gr. 0·970), dried, ignited and weighed as magnesium pyrophosphate.

The re-solution and second precipitation of the ammonium magnesium phosphate is an essential feature of the process, since, in the first precipitation, small quantities of magnesium oxalate are usually formed. The non-observance of this precaution has been a frequent source of high results.

The presence of ammonium citrate and ammonium oxalate results in the retention in solution of a minute quantity of phosphoric acid. It used to be common to precipitate the ammonium magnesium phosphate, in a flocculent form, by the sudden addition of ammonia and magnesia mixture (see, for example, the original directions of Fresenius), and a very substantial correction was then necessary for solubility of the precipitate. Crystalline precipitation, however, reduces this to a minimum, and the accurate determination by molybdic acid of the phosphoric acid in the evaporated and ignited filtrates obtained in a large number of analyses of numerous grades and varieties of phosphate indicates that, if the process is carried out as here described, the quantity of P_2O_5 which escapes precipitation corresponds to an average of approximately 0·0025 g. of $Mg_2P_2O_7$, which quantity must be added to the weight of $Mg_2P_2O_7$ obtained, together with half the weight of the small ammonia precipitate (obtained from the calcium oxalate precipitate), unless this was redissolved into the main filtrate.

Direct Citric-Magnesium Method

In this country, although frequently used for other purposes, this method is officially recognised only in the determination of water-soluble phosphoric acid in superphosphates or compound fertilisers.

To the solution containing phosphoric acid, a relatively large quantity of citric acid is added (with a view to inhibiting subsequent precipitation of calcium, iron or aluminium compounds), the solution made alkaline with ammonium hydroxide, and the phosphoric acid precipitated by magnesia mixture. The method answers well for superphosphate and provided that silica is eliminated by preliminary evaporation of the acid solution to dryness, it gives good results with basic slag, probably by reason of a compensatory balance of small positive and negative errors, it being doubtful whether the precipitate which is finally weighed is pure magnesium pyrophosphate, although the results, arrived at under strictly observed conditions, are the same as those given by the molybdate method. In the experience of the writer, however, this method does not give sufficiently accurate results with raw mineral phosphates or at any rate with some varieties of such phosphates, although it is used in some continental countries for that purpose. Although a useful method for routine work in phosphate mines or factories where approximate results suffice, its use is not desirable for the analysis of samples representing cargoes of large size and consequently of large value where great accuracy is consequently essential.

The method as applicable to basic slag is referred to later (p. 532), and as applied to the determination of soluble phosphoric acid will be found detailed on pp. 522 and 525.

The determination of other constituents of mineral phosphates, viz., iron oxide, aluminium oxide, and fluorine, is dealt with on pp. 542-49.

It is usual to state the results of an analysis of raw mineral phosphate on a "dry" basis, viz., as percentage of the finely ground phosphate dried to constant weight at 100°. In the sampling of cargoes of mineral phosphates, it is usual to grind a substantial quantity of the cargo (usually 1 per cent. of the total weight) to fine flour in the mill of the factory at which it is delivered and to draw from this an average sample for chemical analysis. A separate sample of the phosphate only roughly crushed is taken for determination of moisture.

2. SUPERPHOSPHATE

In considering the analysis of superphosphate and of the various compound fertilisers of which it is an ingredient, it is convenient to reproduce here the current regulations of the Ministry of Agriculture[1] relating to the determination of both soluble and insoluble phosphoric acid in such materials.

[1] *Fertilisers and Feeding Stuffs Regulations*, Ministry of Agriculture, 23rd May 1928.

(iv) *Determination of Phosphoric Acid.*

(a) *Soluble Phosphoric Acid.* Twenty g. of the sample shall be continuously agitated for thirty minutes in a litre flask with 800 millilitres of water at room temperature. The flask shall then be filled to the mark and shaken and the contents shall be filtered.

(A) Fifty millilitres of the filtrate shall be boiled with 20 millilitres of concentrated nitric acid and the phosphoric acid shall be determined by the molybdate method prescribed in paragraph (iv) (d). In the case of fertilisers in which the proportion of phosphoric acid soluble in water is small, a larger quantity of the filtrate prepared as above shall be taken.

(B) *Alternative method.*—Fifty millilitres of the filtrate shall be boiled with 20 millilitres of concentrated nitric acid, cooled, and the excess of acid neutralised with ammonia. Fifty millilitres of ammonium citrate solution, prepared as described below, shall be added and the mixture raised to boiling point. Magnesia mixture shall then be added in the manner prescribed in paragraph (iv) (d).

(b) *Insoluble Phosphoric Acid.* The quantity of soluble phosphoric acid as determined in paragraph (iv) (a) shall be deducted from the quantity of phosphoric acid as determined in paragraph (iv) (c), and the difference, if any, shall be taken as the quantity of insoluble phosphoric acid.

(c) *Total Phosphoric Acid.*

(A) A weighed portion of the sample shall be heated with concentrated sulphuric acid until all organic matter is destroyed and the phosphoric acid is completely in solution. After dilution the solution shall be filtered, the insoluble matter thoroughly washed and the filtrate made up to a definite bulk. The phosphoric acid shall be determined by the method prescribed in paragraph (iv) (d), in an aliquot part of the solution, which shall first be nearly neutralised and then acidified with nitric acid. The insoluble matter is to be washed from the filter, re-extracted with acid and any phosphoric acid present in the solution added to the main quantity.

(B) *Alternative method.*— A weighed portion of the sample shall be incinerated or otherwise treated to destroy organic matter, if present. When direct incineration is employed, the weighed portion of the sample shall be treated, before being heated, with a nitrate or other oxidising

material to prevent loss of phosphoric acid during heating or subsequent treatment. The residue (or the weighed portion taken, if no organic matter is present) shall be dissolved in hydrochloric acid, with the addition, if necessary, of nitric acid, and the solution shall be evaporated to dryness or, if much calcium is present, to a syrupy consistency to fix silica. The residue shall be boiled with nitric acid and, when much iron is present, with hydrochloric acid also. After dilution the solution shall be filtered, the insoluble matter thoroughly washed and the filtrate made up to a definite bulk. The phosphoric acid shall be determined in an aliquot part of the solution by the method prescribed in paragraph (iv) (d). The insoluble matter is to be washed from the filter, re-extracted with acid and any phosphoric acid present in the solution added to the main quantity.

(d) *Molybdate Method.* To the solution, which should contain not more than 0·4 g. of phosphoric acid (P_2O_5), and preferably from 0·1 to 0·3 g., obtained as above described in paragraphs (iv) (a) (A) or (c), 100 to 150 millilitres of molybdic acid solution prepared as described below, or an excess of such solution, *i.e.*, more than is sufficient to precipitate all the phosphoric acid present in the solution, shall be added, and the vessel containing the solution shall be placed in a water-bath maintained at 70° C. for fifteen minutes or until the solution has reached 70° C. It shall then be taken out of the bath and allowed to cool and the solution shall be filtered, the phospho-molybdate precipitate being washed several times by decantation and finally on the paper with 1 per cent. nitric acid solution. The filtrate and washings shall be mixed with more molybdic acid solution and allowed to stand for some hours in a warm place in order to ascertain that the whole of the phosphoric acid has been precipitated. The phospho-molybdate precipitate shall be dissolved in cold 2 per cent. ammonia solution, prepared as described below, and about 100 millilitres of the ammonia solution shall be used for the solution and washings. The solution shall be raised to the boiling point, the beaker removed from the burner and 15 to 20 millilitres of magnesia mixture, prepared as described below, or an excess of such mixture, *i.e.*, more than sufficient to precipitate all the phosphoric acid present, shall then be added drop by drop, with constant stirring. The stirring shall be continued at intervals so long as the

liquid remains very warm. After standing at least four hours with occasional stirring, the precipitate shall be filtered off, washed with 2 per cent. ammonia solution until free from chloride, dried, and finally weighed as magnesium pyrophosphate. The filtrate and washings should not exceed 200 millilitres, and are to be tested by the addition of more magnesia mixture.

(e) *Preparation of Molybdic Acid Solution.* The molybdic acid solution shall be prepared as follows:—

125 g. of molybdic acid and 100 millilitres of water shall be placed in a litre flask and the molybdic acid shall be dissolved by the addition, while the flask is shaken, of 300 millilitres of 8 per cent. ammonia solution, prepared as described below. 400 g. of ammonium nitrate shall be added, the solution shall be made up to the mark with water and the whole added to 1 litre of nitric acid (specific gravity 1·19). The solution shall be maintained at about 35° C. for twenty-four hours and then filtered.

(f) *Preparation of Magnesia Mixture.* The magnesia mixture shall be prepared as follows:—

110 g. of crystallised magnesium chloride and 140 g. of ammonium chloride shall be dissolved in 1300 millilitres of water. This solution shall be mixed with 700 millilitres of 8 per cent. ammonia solution and the whole shall be allowed to stand for not less than three days and shall then be filtered.

(g) *Preparation of the Ammonia Solutions.* The 8 per cent. ammonia solution shall be prepared as follows:—

One volume of ammonia solution of specific gravity 0·880 shall be mixed with three volumes of water. This solution shall then be adjusted by the addition thereto of more strong ammonia solution or water as required until the specific gravity of the solution is 0·967.

The 2 per cent. ammonia solution shall be prepared as follows:—

One volume of 8 per cent. ammonia solution shall be mixed with three volumes of water.

(h) *Preparation of Ammonium Citrate Solution.* 110 g. of pure citric acid shall be dissolved in water, the solution treated with 400 millilitres of 24 per cent. ammonia of specific gravity 0·9135 and then diluted to one litre.

Water-Soluble and Insoluble Phosphoric Acid

Although the foregoing official regulations are now binding upon analysts for legal purposes in this country, it was customary in England for many years prior to the first Fertilisers and Feeding Stuffs Act to separate the water-soluble from the insoluble phosphoric acid in superphosphates and compound fertilisers by fractional extraction with water, finally washing the undissolved matter with boiling water. The dissolved phosphoric acid was then determined in the total filtrate and the insoluble phosphate in the undissolved matter after ignition. It was usual on the Continent, however, to determine the soluble phosphate by agitating a larger quantity of the fertiliser with a given bulk of water, filtering and taking an aliquot part of the solution as representing the "soluble" phosphate. This method was finally adopted by international convention and was made official in England under the last Fertilisers and Feeding Stuffs Act in 1906 and has since been generally adopted, except in America, where a modification of the original fractional method of extraction is still officially used.

The "international" method of extraction as described on p. 522 is to agitate the superphosphate or other fertiliser with water in a strong litre flask, the end-over-end rotatory Wagner machine (see under basic slag, p. 534) being the most convenient for the purpose. The operation is conducted at "room temperature," but this should not be below 17°. After the period of agitation the contents of the flask are made up with water to the litre mark, well shaken and rapidly filtered through a large "fluted" filter, and the phosphoric acid determined in an aliquot part of the filtrate. This portion, which may be 50 or 100 c.c.,[1] is then boiled with 20 c.c. of concentrated nitric acid in order to convert into the ortho-form any phosphoric acid that may be present in the "pyro"-form, as it sometimes is in superphosphate that has undergone a drying process. The phosphoric acid is then determined by the molybdate process, as already described (p. 523); or, alternatively, the solution after boiling with nitric acid is neutralised with ammonia, 6 to 12 g. of pure citric acid added (according to whether 50 c.c. or 100 c.c. has been taken); or (as prescribed in the Regulations of the Ministry of Agriculture) an equivalent quantity of ammonium citrate solution. Excess of ammonia is then added, the mixture heated to boiling, and magnesia mixture added drop by drop, further treatment being as indicated later under basic slag (see p. 533).

These alternative processes give concordant results, and the latter is usually considered preferable where time is a consideration.

In what is sometimes known as "Double Superphosphate," or,

[1] The official regulations of the Ministry of Agriculture prescribe 50 c.c.

generally speaking, in concentrated superphosphates containing 20 per cent. or upwards of water-soluble phosphoric acid, it is now customary on the Continent to vary the foregoing procedure by allowing a longer time of extraction with water. Twenty g. of the double or concentrated superphosphate is placed in the litre shaking flask into which is introduced, not 800 c.c. of water as in the ordinary way, but a larger volume of water, viz., nearly enough to reach to the neck of the flask, giving only sufficient space for free agitation. The flask, after initial shaking, is allowed to stand for twenty-four hours with further occasional shaking. Finally it is made up to the litre mark, once again thoroughly shaken and filtered. With double superphosphates it is even more necessary to boil the aliquot portion of filtrate taken for analysis with nitric acid than when ordinary superphosphate is being examined, for soluble phosphoric acid in a lower state of hydration than that of the ortho-form is usually more abundant. When it is necessary in superphosphate to estimate also the "insoluble" phosphoric acid, the total phosphoric acid is determined, the difference between this and the water-soluble giving the "insoluble" phosphoric acid. For total phosphoric acid, 2 g. of the superphosphate sample may be evaporated to dryness with hydrochloric acid, and the total phosphoric acid determined as already indicated for raw mineral phosphate. Alternative methods of preparation prior to determination of total phosphoric acid in fertilisers containing organic matter are prescribed in the regulations of the Ministry of Agriculture already given (see pp. 522-23).

American Method for Soluble Phosphoric Acid. The fractional method of extraction for water-soluble phosphate, abandoned in England, is still used in America as follows:[1]—

"Place 2 g. of the sample on a 9 cm. filter and wash with successive small portions of water, allowing each portion to pass through before adding more, until the filtrate measures 250 c.c. If the filtrate is turbid, add 1-2 c.c. of strong nitric acid. Dilute to a convenient volume and mix well." (Nothing is said about boiling with acid to ensure all P_2O_5 being in the ortho-form.)

The directions proceed to prescribe the determination of the phosphoric acid in the solution by the molybdate process.

Citrate-Soluble Phosphoric Acid

In superphosphate which has been kept for some time, some of the original water-soluble phosphoric acid is apt to "revert" to the insoluble form of di-calcium di-hydrogen phosphate or a corresponding

[1] *Methods of Analysis of Amer. Assoc. Off. Agric. Chemists*, 2nd edition, 1925, p. 4.

form in which iron or aluminium may replace calcium. This "reverted" or, as it is sometimes called, "precipitated" phosphate may be approximately separated from the originally undissolved tricalcium phosphate by extraction with an alkaline solution of ammonium citrate, and though this form of phosphate is not officially recognised in England, "reverted" phosphate in superphosphate is in some continental countries accepted as being of a value equivalent to that of water-soluble phosphate, and contracts for superphosphate are then based on joint solubility in water and ammonium citrate instead of in water only. Furthermore it is occasionally of moment in aiding the analyst to judge whether a shortage in water-soluble phosphoric acid in superphosphate that has been long in store is attributable to original defect in manufacture or to subsequent change by "reversion."

Precipitated di-calcium phosphate, largely produced as a bye-product in the manufacture of glue from bones, is also sold on the Continent on the basis of citrate solubility.

The results of this determination are to a considerable extent dependent upon the mode in which the operation is carried out. Many empirical methods of distinguishing "citrate soluble" from total phosphoric acid have been from time to time put forward, and as different processes give materially different results, it is necessary that, whichever empirical process may be chosen, the prescribed details should be precisely followed, the particular method used being cited on the analysis certificate in order to allow of its correct commercial interpretation. On the Continent the method now in use is usually Petermann's method, which is based upon the use of strongly alkaline ammonium citrate, while in America, on the other hand, neutral ammonium citrate is officially prescribed. In Germany for many years, in accordance with the suggestions of Wagner, an acid solution of ammonium citrate was in use, especially for the examination of basic slag, but Wagner, himself, for this purpose at any rate, abandoned the use of ammonium citrate, substituting for it a 2 per cent. solution of citric acid, as described, in connection with basic slag. (See p. 533.)

Only the "alkaline" method of Petermann and the "neutral" method in use in America will be here described.

Alkaline Citrate Method (Petermann).—The citrate solution is prepared as follows:—Five hundred g. of citric acid is dissolved in water, neutralised by ammonia, the solution cooled, diluted to a sp. gr. 1·09, and ammonia of sp. gr. 0·92 added to the extent of 50 c.c. of ammonia per 1 litre of solution; the specific gravity of the final solution is 1·082 to 1·083.

In the case of superphosphate or other acid fertiliser 2·5 g. of the sample (or more if the phosphoric acid concentration is low) is triturated gently in a glass or porcelain mortar with successive

quantities of 20 to 25 c.c. of water, the settled liquid being each time decanted on to a paper filter and collected in a 250 c.c. flask. The operation is repeated at least three times, the undissolved matter being finally brought on to the filter and washed until the liquid in the flask measures about 200 c.c. This liquid is then cleared with a few drops of nitric acid and made up to 250 c.c. The filter and solid residue are then placed in a 250 c.c. flask, 100 c.c. of ammonium citrate solution added, and the flask allowed to stand for fifteen hours at the ordinary temperature, with occasional shaking. The mixture is then digested on the water-bath for one hour at 40°, filled up to the mark when cold, and filtered; 50 c.c. of the filtrate, and 50 c.c. of the aqueous solution first prepared are then taken and mixed, the mixture boiled for ten minutes with 10 c.c. of concentrated nitric acid, and the total phosphoric acid soluble in water, plus that soluble in citrate solution, determined in this solution either by the molybdate or citrate method.

The method, it may be added here, is frequently applied to precipitated bone phosphates, when 1 g. of the sample is triturated in a mortar several times with successive quantities of Petermann solution, the decantations being collected in a 500 c.c. flask into which the undissolved matter is finally washed with further quantities of the citrate solution until 200 c.c. of solution in all have been used. The flask and its contents are then allowed to stand over night, heated on a water-bath at 40° for one hour, cooled, made up to 500 c.c. with water, well shaken and filtered. An aliquot part of the solution is then boiled with nitric acid and the phosphoric acid determined by the molybdic method.

American Neutral Citrate Method.—In America alternative directions are given for the preparation of the neutral ammonium citrate solution,[1] preference being indicated for the following:—

> For every litre of solution required dissolve 172 g. of anhydrous or 188·13 g. of crystallised citric acid in approximately 700 c.c. of water; nearly neutralise with strong ammonium hydroxide; cool; measure the volume of the solution or make it up to a convenient volume, taking care to keep the density above 1·09; and make exactly neutral, testing as follows:—
>
> With a pipette transfer 5 c.c. of the citrate solution to a test tube (7 × 7/8 inches is a convenient size) and dilute to 20 c.c. with water. Add from a dropping bottle 5 drops of a 0·08 per cent. solution of phenol red indicator, either an alcoholic solution of the dye or an aqueous solution of its alkali salt being suitable. From a burette run in approximately 2 *N* ammonium hydroxide until the colour approximates that of a standard buffer solution

[1] *Off. Methods of Anal. Amer. Assoc. Agric. Chem.*, 1924, p. 4.

having a *p*H of 7·0 contained in a similar test tube and with the same concentration of indicator. (This buffer solution may be prepared by mixing 50 c.c. of 0·2 *M* dihydrogen potassium phosphate solution, *i.e.* a solution of 27·22 g. of KH_2PO_4 per litre, and 29·63 c.c. of *N*/5 sodium hydroxide solution and making up to 200 c.c. Chemicals especially purified for this purpose should be employed, and the standard buffer solution finally used should not have stood more than a few days unless some method of checking its reaction is available.) From the quantity of ammonium hydroxide solution required to produce in the sample a colour that exactly matches that of the standard, the quantity required to neutralise the rest of the solution is calculated. This calculated quantity of ammonium hydroxide is added to the original solution and its reaction again checked against that of the neutral standard. When the solution has thus been accurately neutralised, it is diluted to a density of 1·09 at 20°.

In the case of acid fertilisers, superphosphate, etc., the water-soluble phosphate is first extracted by the fractional process (washing on a filter as already described). One hundred c.c. of the ammonium citrate solution is raised to a temperature of 65° in a 250 c.c. flask and the filter containing the water-insoluble matter from the fertiliser is dropped into the solution and the flask which is closed with a rubber stopper shaken vigorously until the filter paper is reduced to a pulp. The flask is returned to the water-bath and maintained at a temperature of 65° for half an hour, being shaken every five minutes. The contents of the flask are then filtered as rapidly as possible through a quick-acting filter, the undissolved matter being washed with water at 65° until the filtrate measures about 350 c.c., allowing thorough draining between each washing. The phosphoric acid is then determined in the insoluble residue.

In the case of non-acid fertilisers, 2 g. of the fertiliser is introduced into the citrate solution without previous washing by water, the operation otherwise being as described for acid fertilisers.

In either case the citrate soluble phosphate is obtained by deducting the phosphoric acid undissolved by the citrate solution from the total phosphoric acid separately determined.

Free Phosphoric Acid

It is sometimes necessary to determine free phosphoric acid in superphosphate as distinguished from mono-calcium tetra-hydrogen phosphate.

Gravimetric Method. Ten g. of superphosphate is thoroughly extracted in a Soxhlet apparatus with dry ether, which dissolves free phosphoric acid, though somewhat slowly, leaving behind the mono-calcium tetra-hydrogen phosphate. The ether is evaporated and the phosphoric acid determined in the residue. The superphosphate should be dried for a short time in a water oven before extraction.

Volumetric Method. The method originally adopted by the Union of German Manure Manufacturers is still in use. It is based upon titration of an aqueous solution of the superphosphate with sodium hydroxide, using methyl orange as an indicator, free phosphoric acid being acid to the extent of one of its three atoms of hydrogen as regards this particular indicator. Unfortunately the reaction is vitiated by the fact that it is difficult, if not impracticable, to carry out the titration with sodium hydroxide without incidentally forming some precipitate of di-calcium di-hydrogen phosphate when a large excess of mono-calcium tetra-hydrogen phosphate, as well as of calcium sulphate, is present. The description of the method is accompanied by recommendations as to details of procedure directed to the diminution of the error thus incidentally introduced, but the method is not satisfactory.

Schucht, in his very comprehensive work on the manufacture of superphosphate,[1] discusses the determination of free phosphoric acid and describes a fairly simple method of his own for obviating the errors incidental to titration by converting all soluble calcium salts into the corresponding potassium salts.

The solution obtained for the determination of water-soluble phosphoric acid by the International method of shaking up 20 g. of superphosphate with water and making up to 1 litre is used. In 100 c.c. of the filtered solution, the total calcium is determined (which may be rapidly and conveniently effected by adding first a little citric acid, then a slight excess of ammonia, finally excess of acetic acid, boiling the solution and precipitating with excess of ammonium oxalate; the ammonium oxalate being filtered, washed, dried, and either ignited to calcium oxide in a muffle or, preferably, converted into calcium carbonate by gentle ignition over a yellow Argand flame).

To 500 c.c. of the main filtered solution, sufficient pure crystallised potassium oxalate ($K_2C_2O_4, H_2O$) is added to precipitate the whole of the calcium in the solution, the quantity required being calculated from the calcium ascertained to be present in solution. In this way the original mono-calcium tetra-hydrogen phosphate is converted into the corresponding potassium salt and the calcium sulphate into potassium

[1] *Die Fabrikation des Superphosphats*, by Ludwig Schucht, 3rd ed., 1909.

sulphate, while the free phosphoric acid remains unchanged. After allowing to settle, the liquid is filtered and to 200 c.c. of the filtrate 10 g. of sodium chloride is added and the free phosphoric acid titrated with standard $N/10$ sodium hydroxide solution using methyl orange as indicator. Each c.c. required corresponds to 0·0098 g. H_3PO_4 or 0·0071 g. of "free" P_2O_5.

The writer has slightly modified Schucht's procedure by substituting, as just described, the necessary weight of crystalline potassium oxalate for a corresponding volume of a normal solution thereof, thus somewhat simplifying the incidental calculations.

Moisture in Superphosphate.—The old conventional method of drying to constancy in a water or steam oven at 100° is still generally followed, although, as was first pointed out by Ruffle,[1] in 1887, the figure obtained does not represent moisture in the sense of dampness, for it includes water present in the form of water of crystallisation combined with calcium sulphate. Ruffle proposed to substitute the more rational method of drying at the ordinary temperature under reduced pressure over calcium chloride, but the method, although favourably received at the time, fell into abeyance, and loss of weight at 100° is still commonly accepted as "moisture."

3. BASIC SLAG

Basic slag, however well ground, usually contains some fragments of metallic iron which cannot be powdered in a mortar, and so cannot be regularly distributed and properly represented in the portion taken for analysis and must therefore be removed.

If "fine meal" is to be determined, a fair average portion of the sample, in the state in which it is received, must first be taken for this purpose. The remainder is weighed and, as far as possible—with the aid of hand grinding in an iron mortar—passed through a fine sieve. The fragments of iron, which do not pass the sieve, are weighed, the percentage of phosphoric acid subsequently found by analysis being adjusted by calculation so as to represent the original sample inclusive of the separated iron fragments. These fragments of iron commonly amount to a few tenths of 1 per cent., but there may be 1 per cent. or more. If the fragments of iron are not removed, the inclusion or exclusion of a portion of them, in the quantity of slag weighed out for analysis, may appreciably affect the accuracy of the result, and there is reason to suppose that, in badly ground slag, the overlooking of this source of error by analysts has sometimes been the cause of discrepancies.

[1] *J. Soc. Chem. Ind.*, 1887, 6, 327.

Total Phosphoric Acid

The total phosphoric acid in basic slag is determined by some modification of the molybdate process, or alternatively by direct magnesium precipitation without removal of calcium. The most fruitful sources of error are due to the vitiating effects of soluble silica, and to the difficulty, unless special precautions are taken, in removing by acid solvents the last traces of phosphoric acid from the matters primarily undissolved by acid. Rapid methods of solution in hydrochloric or nitro-hydrochloric acid are apt to exaggerate the last-named difficulty, and after evaporation to dryness with hydrochloric acid or nitro-hydrochloric acid and re-solution, the siliceous residue, even after well washing, is apt to retain some phosphoric acid which it is necessary to extract by boiling the siliceous residue again in strong hydrochloric acid. The method frequently adopted of merely boiling a quantity of slag with hydrochloric or nitro-hydrochloric acid, "making up to bulk" and taking an aliquot part of the solution, ignores this error and is consequently apt to give low results. In some slags this source of error is negligible, but in others it may assume serious proportions.

Molybdate Method.—If this is to be used for slag, as is now obligatory in this country for official analysis under the Fertilisers and Feeding Stuffs Act (see pp. 522-23), the most reliable and convenient solvent for the phosphoric acid is sulphuric acid. A weighed quantity of the slag is heated on a hot plate with sufficient of a mixture of equal volumes of water and concentrated sulphuric acid to well cover it. The heating is continued until the liquid emits fumes of sulphuric acid. It is then cooled, diluted with water, filtered and washed with boiling water.

The writer uses 2 g. of slag and determines the phosphoric acid in the whole of the solution derived from it; but alternatively, as in the official directions of the Ministry of Agriculture (see p. 523), the solution of a larger quantity may be made up to a definite bulk and an aliquot part of the solution taken for the determination. In either case the solution is acidified with nitric acid and precipitated with molybdate, the precipitate being dealt with according to the directions of Jörgensen, which are epitomised in the official directions of the Ministry (see p. 523).

Direct Citrate-Magnesium Method.—If correct results are to be obtained, the soluble silica must be eliminated by complete evaporation to dryness of the acid solution. The following procedure is recommended:—

Two g. of slag is treated with a considerable excess of strong hydrochloric acid, evaporated to dryness, taken up again with a little

strong hydrochloric acid, warmed, diluted with hot water and filtered. The undissolved matter after well washing with acidulated hot water is redigested in a further portion of strong hydrochloric acid for some time on a hot plate, filtered and the filtrate added to the main filtrate. Twenty g. of citric acid is added to the filtrate followed by a quantity of magnesia mixture in excess—say 45 c.c. Ammonia is then added drop by drop, while the mixture is rapidly and continuously stirred. Stirring is continued by means of a mechanical stirring apparatus for fifteen minutes, after which, with further occasional stirring, the mixture is allowed to stand for two hours. The precipitate is then filtered, washed with 2 per cent. ammonia solution, ignited and weighed, the precipitate being assumed to have the composition of magnesium pyrophosphate. There is an element of empiricism in the process, and it is doubtful whether in all cases the precipitate has the exact constitution assigned to it, or whether, as has been previously suggested, it may not sometimes owe the fact that it contains the theoretical proportion of P_2O_5 to a balance of small ± errors. However this may be, the process, if thus carried out with basic slag, gives results which agree in practice with those of the more scientific molybdate method within the limit of tolerance practically obtainable in duplicate analyses by the molybdate process itself. The more rapid method of merely boiling the slag with strong nitric or hydrochloric acid, or a mixture of the two, without evaporation to dryness, making up to bulk, and taking an aliquot portion which is frequently adopted, is liable to introduce grave errors owing to the retention of silica in solution and resulting contamination of the final precipitate.

Citric Acid Soluble Phosphate

For many years it has been usual in addition to the total phosphoric acid to determine in basic slag the proportion of phosphoric acid soluble in citric acid. An acid solution of ammonium citrate originally recommended by Wagner was formerly used, but this solution soon gave place to his later recommendation of a solvent consisting of a 2 per cent. solution of citric acid without any ammonium citrate.

In the recent regulations of the English Ministry of Agriculture made under the new Fertilisers and Food Stuffs Act, citric acid solubility (although recognised under the earlier Act) has ceased to be officially recognised in England; but the buyers of basic slag here, as on the Continent, still usually demand a statement of the citric-acid-soluble as well as of the total phosphoric acid, in view of the fact that different makes of slag vary very much in "citric solubility," and of the still extant view that "citric solubility" furnishes some approximate index of the probable comparative rapidity of action in the soil, if not necessarily of ultimate availability. This view is not without its

opponents and the matter cannot be discussed here. The agricultural analyst is thus very frequently called upon to state, in addition to the total phosphoric acid, the proportion soluble in citric acid. Wagner's procedure, which should be closely followed as regards method of extraction, is as follows:—

Five g. of the slag is placed in a litre shaking flask and moistened with 5 c.c. of alcohol (to prevent caking), 10 g. of pure crystallised citric acid dissolved in 495 c.c. of water is poured into the shaking flask, which is closed with an indiarubber bung and agitated for thirty minutes in a mechanical "end over end" shaking apparatus. The form of shaking apparatus commonly used is that devised by Wagner, and is to be found listed in the catalogues of leading makers of chemical apparatus. The operation is usually carried out at what is called "room" temperature, but it is desirable that this should not fall below 17°. The rotation apparatus should, therefore, if practicable, be set up in a room of approximately constant temperature. The revolutions of the machine should be from 30 to 40 per minute. After thirty minutes' agitation, the liquid is rapidly filtered through a large folded filter and an aliquot part of the solution taken for the determination of dissolved phosphoric acid. This determination may be carried out by the molybdate process or by "direct" precipitation by the citrate magnesium process. The determination by either method, however, is liable to serious error if the dissolved silica is not first eliminated. The liability to error is greater with some slags than with others, as the quantity of silica dissolved by the citric acid solution varies.

When direct precipitation with magnesia mixture is to be adopted, the measured quantity of citric acid solution is evaporated to dryness in a water-bath with hydrochloric acid. The writer prefers to evaporate 200 c.c. of the solution representing 2 g. of slag. After evaporation, the residue is taken up with strong hydrochloric acid followed by addition of water; the silica is filtered off, thoroughly washed with acidulated hot water and the filtrate precipitated with magnesia mixture exactly as already described for the direct determination of total phosphoric acid in slag (p. 533).

If the molybdate process is to be used, the residue of the measured portion of citric acid solution, after evaporation to dryness in the water-bath with hydrochloric acid, is taken up with diluted sulphuric acid (1 in 4 by measure), heated to boiling, diluted and filtered. The silica is thoroughly washed on the filter paper with boiling water and is then boiled with a little dilute nitric acid, filtered, re-washed and tested separately with molybdate solution to make sure that all traces of phosphoric acid have been washed out. The result is usually negative, but this precaution should not be overlooked.

VOLUMETRIC METHODS OF ESTIMATING PHOSPHORIC ACID

Uranium Method

This method was at one time largely used and may be still (though probably rarely) in use in works' laboratories for obtaining rapid approximate results for comparative purposes. It is based on the precipitation with a standard solution of uranium nitrate or uranium acetate in an acetic acid solution.

The solution containing the phosphoric acid to be estimated is made first alkaline with ammonia and then acidified with acetic acid. Since iron and aluminium phosphates are either in whole or part precipitated, the uranium titration ignores such of the phosphoric acid as may be contained in this precipitate. The standard uranium solution is progressively added, with stirring, until a drop of the liquid brought into contact with a drop of weak potassium ferrocyanide solution (or a speck of powdered potassium ferrocyanide) on a white porcelain tile produces a reddish-brown coloration indicating excess of uranium.

The uranium solution may be made by weighing out 36 g. of crystallised uranium nitrate or 30 g. of uranium acetate, adding 5 c.c. of glacial acetic acid, dissolving in water and diluting to 1 litre. One c.c. of such a solution will be equivalent to rather more than 0·005 g. P_2O_5. The uranium solution may be standardised by titrating (after addition of ammonium acetate) a measured portion of a nitric acid solution of tricalcium phosphate of known strength. The tricalcium phosphate used for making the solution is repurified by solution in acid, precipitation by ammonia, thorough washing and final ignition. Of this approximately pure tricalcium phosphate 5·5 g. is dissolved in the least possible quantity of nitric acid and the solution made up to a litre. In a portion of this solution the quantity of phosphoric acid actually present is checked by a gravimetric determination, and its phosphoric acid content being thus accurately known, further portions of 50 c.c. (after addition of ammonium acetate) are titrated as already indicated, with the uranium solution. The strength of the latter having been ascertained, it is convenient to readjust it by dilution so that 1 c.c. is equivalent to 0·005 g. P_2O_5.

In rapid routine factory analyses, where materials of approximately known composition are dealt with, the error due to the presence of iron and aluminium has sometimes been empirically allowed for; but if the method is to give even approximately accurate results the solution of phosphate must first be boiled with ammonium acetate and the precipitate of iron and aluminium phosphates filtered off, the old practice having been to wash, dry and ignite the precipitate and to

assume that half of it is phosphoric acid. This assumption, however, is incorrect, as the precipitate will frequently contain some calcium phosphate and even after thorough washing is usually basic in composition, so that if a really accurate result is to be looked for, the ammonium acetate precipitate must be analysed (see p. 544). Obviously the additional work thus represented removes any advantage derived from the speed of the uranium titration. Even at the best it is an unsatisfactory process, and where rapid results are required in a factory, it has now been generally abandoned in favour of some form of volumetric molybdate process.

Volumetric Molybdate Process

Pemberton,[1] in 1893 (following Hundeshagen[2]), assumed a constant composition for the yellow precipitate formed at about 70°, and concluded that when the precipitate was dissolved in and accurately neutralised by sodium hydroxide solution each c.c. of $N/10$ sodium hydroxide used in neutralising the washed yellow precipitate was equivalent to 0·002842 g. P_2O_5. It has been shown, however, that the neutralising power or acid equivalent of the yellow precipitate depends on the temperature at which it is formed. There have been various modifications of the process which under prescribed conditions has been accepted as an alternative official process in the analysis of fertilisers in the Official American Methods.

In the directions there given,[3] an acid solution of the fertiliser is made up to bulk and an aliquot portion of the solution taken, corresponding to 0·4 g. for materials containing not more than 5 per cent. of P_2O_5; to 0·2 g. where the percentage ranges from 5 to 20; or 0·1 g. where the percentage exceeds 20. Five to 10 c.c. of strong nitric acid is added, then ammonium hydroxide, until the precipitate at first formed just redissolves, after which the liquid, diluted to from 75 to 100 c.c., is warmed on a water-bath to a temperature of from 45° to 50°. Molybdate solution is added in sufficient quantity to secure complete precipitation and the mixture is maintained at the above temperature for thirty minutes. The supernatant liquid is decanted through a filter, the precipitate washed twice by decantation with water (thoroughly agitating each time) and is then transferred to the filter and washed with cold water until the filtrate from two fillings of the filter yields a pink colour on addition of phenolphthalein, and one drop of weak alkali of the strength to be used for titration.

The precipitate and its filter are then transferred to the precipitating beaker and the precipitate dissolved in a small excess of standard

[1] *J. Amer. Chem. Soc.*, 1893, **15**, 382; 1894, **16**, 278; and 1895, **17**, 178.
[2] *Z. anal. Chem.*, 1889, **28**, 141.
[3] *Off. Methods of Anal. Assoc. Agric. Chem.*, 1925.

alkali. The standard alkali, either sodium or potassium hydroxide, is of such a strength that 100 c.c. is neutralised by 32·38 c.c. of *N* acid. The yellow precipitate being dissolved in excess of this standard alkali, phenolphthalein is added and the excess of alkali titrated with standard acid. Each c.c. of the special standard alkali neutralised by the phosphomolybdate precipitate is taken to represent 1 mg. of P_2O_5. If, for purposes of comparison with Pemberton's assumption, the strength of this alkali is worked out into the usual decinormal notation, the equivalent assumption is that 1 c.c. *N*/10 alkali = 0·0003008 P_2O_5.

The process was critically investigated in 1914 by J. A. Prescott,[1] mainly in relation to its application in soil analysis. To about 100 c.c. of the acid solution of phosphate he adds 25 c.c. of a concentrated solution of ammonium nitrate (500 g. ammonium nitrate and 1 litre of water) and a sufficiency of molybdate solution, raising the temperature to 55° in a water-bath and allowing the liquid to cool for two hours. The liquid is filtered and the precipitate washed by decantation several times with a 2 per cent. solution of sodium nitrate, the washing being continued till the washings are no longer acid. The precipitate with its filter is titrated in a beaker with excess of *N*/10 alkali and the excess titrated with acid, using phenolphthalein as indicator. Prescott found that 1 c.c. *N*/10 alkali = 0·0003004 P_2O_5.

N. D. Ridsdale, in 1919,[2] suggested a modification of Pemberton's method for use in steel analysis. After addition of excess of permanganate and reduction with oxalic acid, the solution containing the phosphoric acid was heated to boiling and cold molybdate solution added, the mixture being shaken for two minutes, allowed to stand at about the temperature of the laboratory from five to fifteen minutes, after which the filtered and washed precipitate was titrated with sodium hydroxide, the final calculation being based upon the assumption that 1 c.c. of *N*/10 sodium hydroxide was equivalent to 0 0002978 P_2O_5.

Ridsdale's modification has been recently investigated and developed for use in fertiliser analysis by Cameron and Dow.[3] The nitric acid solution of the fertiliser, previously freed from organic matter, is nearly neutralised with sodium hydroxide solution, reacidified with nitric acid, and permanganate solution added until permanent coloration occurs. A mixture of ammonium nitrate, chloride and oxalate is added, the latter decolorising the permanganate. The liquid is heated to boiling and excess of molybdate added. After shaking, the liquid is set aside for ten minutes and decanted through a filter funnel plugged with cotton wool. The precipitate is washed into a Nessler tube and

[1] *J. Agric. Sci.*, 1914, **6**, 111. [2] *Chem. News*, 1919, **118**, 100.
[3] *Analyst*, 1927, **52**, 576.

centrifuged with the nitrate solution; this operation is repeated several times, the supernatant liquids being poured through the plugged funnel. The washings are repeated until the filtrates are freed from acidity as indicated by methyl orange. The precipitate is finally titrated with *N*/2 sodium hydroxide solution, 1 c.c. being taken as equivalent to 0·001542 g. P_2O_5. On this assumption 1 c.c. of *N*/10 sodium hydroxide would be equivalent to 0·0003084 g. P_2O_5.

Cameron and Dow give analyses of various fertilising materials, made by their method, which appear to indicate that under the condition in which they work, their titration gives results practically identical with those obtained by accurate gravimetric methods. From what we have here recorded, however, it is evident that the composition of the yellow precipitate (and consequently its alkali equivalent) varies sufficiently, according to the conditions under which it is obtained, to cause substantial variations in the quantity of standard alkali required to neutralise it, and that the empirical conditions laid down in any particular modification of the process must be strictly observed in order to give validity to the results obtained. In work such as soil analysis, where relatively small quantities of phosphoric acid are in question, the method as laid down by Prescott is satisfactory, and (if his conditions are observed) less affected by incidental error than the gravimetric determination.

As regards fertilisers (or their raw materials) which contain large percentages of phosphate, the liability of the precipitate to variation under different circumstances appears to the writer to make any modification of the Pemberton method inadequate when really accurate results are required; but for approximate purposes such as in routine factory analyses, for example, in rapidly determining the phosphoric acid content of successive batches of basic slag, where saving of time is more essential than strict accuracy, the method, standardised for the conditions under which it is to be used, presents obvious advantages over the necessarily slower gravimetric methods.

4. MISCELLANEOUS FERTILISERS

PERUVIAN OR OTHER NATURAL GUANO

Raw guano (the excreta of sea-birds) contains phosphoric acid in various forms, such as calcium and magnesium phosphates not soluble in water, and soluble phosphates of potassium, sodium or ammonium. It is usual, however, to guarantee only the total phosphoric acid with its calculated equivalent as tri-calcium phosphate, without differentiation between that which may be soluble or insoluble in water.

Nitrogen occurs in guano in many forms ranging in structure from feathers down to free ammonia or ammonium carbonate and nitrates,

and including various forms of organic bases and acids such as guanidine, urea and urates. In commercial practice it is usual only to determine the total nitrogen which, if nitrates are present, must be effected by the Jodlbauer modification of the Kjeldahl method described on p. 503. It is usual, as with other fertilisers, to state the quantity of ammonia (NH_3) to which the total nitrogen is arithmetically equivalent.

Potash is determined as prescribed in the official methods under Potash (see p. 552).

Moisture and sand are sometimes also included in the analysis. The former item is conventionally estimated as loss on heating in a water oven. Some ammonia or ammonium carbonate is volatilised with the moisture, and therefore this item should be returned in an analysis as "Moisture (loss at 100° C.)" to prevent misunderstanding.

FISH GUANO (FISH MEAL), WHALE GUANO, MEAT MEAL, BONE MEAL, AND MEAT AND BONE MEAL

In these articles, regarding them here as fertilisers (although some of them are also utilised as feeding stuffs), it is usual to determine the total phosphoric acid, stating also its equivalent as tricalcium phosphate and the total nitrogen and the ammonia to which it is arithmetically equivalent. Moisture (loss at 100°) and sand are sometimes also required to be stated, and in the case of fish guano sometimes also the percentage of sodium chloride.

As regards phosphoric acid, sufficiently accurate results may usually be obtained by making the determination in the ash obtained by simple incineration at a low temperature, but for official purposes, on which legal action may depend, it is necessary, if only *pro formâ*, to observe the more complete directions laid down in the official regulations (see pp. 522-23).

The nitrogen is determined in the usual way, its arithmetical equivalent in ammonia being also stated.

"Organic matter," if returned in the analysis, is taken as loss on ignition after deduction of moisture

DRIED BLOOD, HOOF AND HORN MEAL, WOOLLEN WASTE, SHODDY, LEATHER DUST OR MATERIALS PREPARED THEREFROM, AND VARIOUS NITROGENOUS ORGANIC WASTE MATERIALS.

As a rule the only determinations required are moisture (loss at 100°) and total nitrogen by the methods already set out (p. 496). Sometimes permanganate-soluble nitrogen (Street) has also to be determined (see pp. 508-11).

Compound Fertilisers, such as Dissolved Bones, Corn Manure, Mangolds or Turnip Manure, Grass Manure, etc.

Moisture, as stated, is determined in the usual way by drying at 100°.

The soluble and insoluble phosphoric acid and nitrogen are determined as indicated on pp. 522-23, and potash, if present, as described on p. 552. It is usual to state with both soluble and insoluble phosphoric acid, their calculated equivalents as tri-calcium phosphate.

Precipitated Calcium Phosphate. Total phosphoric acid is determined and sometimes the citrate soluble phosphate by Petermann's method (p. 527).

Calcium Sulphate (*Gypsum, etc.*). The material is dissolved in hydrochloric acid, the silica removed by filtration and the filtrate precipitated with ammonia; the precipitated iron oxide with any alumina (contaminated on the first precipitation with some calcium carbonate) filtered off, washed, redissolved and reprecipitated, again filtered and washed. The filtrate is rendered slightly acid with acetic acid and the calcium determined by precipitation with ammonium oxalate in a boiling solution, the calcium oxalate being filtered, washed, dried, and either ignited at a low temperature and weighed as calcium carbonate, or ignited in a muffle and weighed as calcium oxide. The sulphuric acid is determined in another portion, in the usual way, as barium sulphate.

Sodium Nitrate—Chile Saltpetre (*cf.* Vol. I., pp. 470-486).

Nitrogen is determined by the Devarda or Ulsch method (pp. 505-6). In the experience of the writer the Devarda method is decidedly preferable.

Moisture is determined by gently heating 5 g. of the finely powdered sample in a platinum basin over a very low flame till incipient fusion occurs, cooling and weighing. Alternatively, the finely powdered sample may be dried to constancy in an oven at a temperature of 120°.

Sand and other insoluble matter are determined by solution in water, the well-washed insoluble matter being incinerated and weighed.

Chlorides (calculated as sodium chloride) are determined volumetrically in the usual way by titration of a neutral aqueous solution with standard silver nitrate, using potassium chromate as indicator, or by Volhard's method, viz., precipitation with excess of standard silver nitrate in a nitric acid solution followed by filtration and "back" titration of the excess of silver in the filtered solution with potassium thiocyanate with a ferric salt as indicator. The result is stated as sodium chloride.

Perchlorate is sometimes present in the form of potassium perchlorate and its determination may be required. Various methods have been suggested for this purpose based upon subtraction of the chlorine originally present as chloride (determined as already indicated) from the total chlorine found after reduction of perchlorates or chlorates (if present) to the form of chloride.

The following method due to C. Gilbert[1] is simple and convenient: 10 g. of the finely powdered nitrate is mixed with 2 g. of sodium carbonate and 1 g. of manganese dioxide, the whole being well mixed by grinding in a glass mortar and then heated for about fifteen minutes to a dull red heat in a nickel crucible. The contents are then treated with hot water and the filtered solution, rendered just acid with nitric acid, is precipitated with an excess of $N/10$ silver nitrate, the precipitate filtered off and washed, and the excess of silver titrated with $N/10$ ammonium thiocyanate, using iron alum as an indicator (Volhard). The chlorine thus determined includes both that originally present as chloride and that originally present as perchlorate, and reduced to chloride by the ignition with sodium carbonate and manganese dioxide. From the difference between this total and the chloride as determined by direct titration in the original nitrate, the potassium perchlorate is calculated.

An excellent method for the detection and approximate estimation of perchlorates in sodium nitrate has been devised by A. Monier[2]:—

To 20 c.c. of 5 per cent. solution of the sample is added 1 c.c. of a 0·3 per cent. solution of methylene blue in water, the mixture being left overnight. A deep blue crystalline precipitate forms and the supernatant liquid is tinted blue. The tube and its contents are compared with standard tubes containing various amounts of pure potassium perchlorate similarly prepared. If the perchlorate is present to the extent of less than 0·2 per cent., a 10 per cent. solution of the crude nitrate is used, or if more than 0·5 per cent., a 2·5 per cent. solution is used. Should the sample contain any appreciable quantity of iodide, this must be first removed by shaking the solution with moist silver oxide and filtering.

The test is delicate and the writer finds that a quantitative estimate visually formed by this colour comparison agrees closely with the result of the determination by Gilbert's method, already described. In any case it furnishes a useful confirmatory method.

Sulphates. Sulphuric acid may be determined in the usual way as barium sulphate in a solution of nitrate acidified with hydrochloric acid, the analyst being, of course, on his guard as to the possible initial precipitation of a little barium nitrate from which (if any) the precipitate

[1] *Methoden zur Bestimmung des Perchlorats im Chile-salpeter*, Tubingen, 1899.
[2] *Arch. Sci. phys. nat.*, 1916, **42**, 210; *J. Chem. Soc.*, 1916, **110**, 639.

must be thoroughly freed by ample washing. The sulphuric acid is calculated as sodium sulphate.

Potash. Many samples of sodium nitrate contain substantial quantities of potash (for determination see under Potash Salts, p. 549 *et seq.*).

For trade purposes, as in the valuation of cargoes, it has long been the custom, in England at any rate, to adopt an abbreviated form of analysis in which the items determined are moisture, insoluble matter, sulphate (calculated as sodium sulphate) chloride (calculated as sodium chloride), the difference between these items and 100 being taken as "nitrate." This "difference" method ignores the possible presence of potassium nitrate (as distinguished from sodium nitrate) and also that of potassium perchlorate, and therefore the percentage of nitrogen present, which is the really important feature, cannot be correctly inferred. Under the Fertilisers and Feeding Stuffs Act, the percentage of nitrogen must be stated and is determined in accordance with the official regulations (*cf.* p. 551).

POTASSIUM NITRATE—SALTPETRE OR NITRE

The methods described under sodium nitrate are applicable, the determination of potassium being of course an essential feature of the analysis (see p. 551).

CALCIUM NITRATE

The nitrogen is determined as in sodium nitrate (preferably by the Devarda method), and the calcium as indicated under calcium carbonate, etc. (p. 557).

Determination of Iron and Aluminium Oxides in Mineral Phosphates

The solvent used should be hydrochloric acid rather than *aqua regia*. The latter is sometimes recommended. For many phosphates it is perhaps immaterial which solvent is used. But some phosphates (such as American river pebble phosphates) contain iron pyrites. If *aqua regia* is used, this is dissolved and included as iron oxide—which is misleading, as pyrites is not attacked by the sulphuric acid used in superphosphate making, and is consequently unobjectionable. It should, therefore, be eliminated with the silica, as is the case if hydrochloric acid is used as the solvent.

There are two methods in use which accurately determine iron and aluminium oxides.

Glaser's Method. The method most in use is that of Glaser,[1] which is based upon the insolubility of calcium sulphate in alcohol and the

[1] *Z. angew. Chem.*, 1889, 3, 636.

solubility of iron and aluminium phosphates therein in presence of acid, these phosphates being, after evaporation of the alcohol, precipitated by ammonia and weighed. Glaser originally assumed that the precipitate obtained consisted of orthophosphates of the two metals (in which case the aluminium oxide could be deduced from the total weight of the precipitate after a separate determination of iron); and it has been largely assumed that for commercial analyses one half of the "Glaser precipitate" as weighed may be taken as representing the joint quantity of mixed iron and aluminium oxides contained therein. The latter assumption is obviously empirical, and the former is not correct as there is a tendency for the precipitate of iron and aluminium phosphates to become basic during washing to an extent which varies with the exact conditions under which precipitation and washing are carried out. The following extended modification of Glaser's method may be relied upon as giving accurate results:—

Modified Glaser Method. Four g. of the phosphate is treated with about 25 c.c. of strong hydrochloric acid and evaporated to dryness. The residue is taken up with 10 c.c. of strong sulphuric acid, about an equal bulk of water being cautiously added. After digestion in a water-bath for about fifteen minutes, the cake of calcium sulphate is well broken up by stirring with a glass rod, and the whole contents of the beaker are washed into a 200 c.c. flask with ordinary strong alcohol (methylated spirit), and allowed to remain for an hour with frequent shaking. The contents are then made up (with spirit) to 200 c.c., again well shaken and filtered rapidly. Of the clear filtrate, 100 c.c. (= 2 g. of the sample) is evaporated in a glass or porcelain basin until the residue fumes and begins to "char," when it is washed with a little hot water into a beaker and mixed with sufficient bromine water to colour it strongly. After standing for half an hour, the liquid is heated nearly to boiling and precipitated with slight excess of ammonia, kept in a water-bath for half an hour and made slightly acid with acetic acid. The precipitate (which, under these conditions, contains only phosphoric acid and iron and aluminium oxides) is filtered off, washed with a slightly ammoniacal 20 per cent. solution of ammonium nitrate, dried, ignited and weighed. It is then dissolved in a little hydrochloric acid, 1 g. of citric acid is added to the solution, which is then made ammoniacal, and the phosphoric acid determined by precipitation with magnesia mixture. The total bulk of fluid should not be more than about 100 c.c. The precipitate of ammonium magnesium phosphate does not need re-solution and reprecipitation, as no oxalate is present. The iron is precipitated from the filtrate with ammonium sulphide. If allowed to stand for an hour or two at a temperature of about 80°, the precipitate settles well and may be rapidly filtered, washed with hot water to which a little ammonia and

ammonium sulphide are added, ignited strongly and weighed as Fe_2O_3. The weight of the ammonia precipitate minus its phosphoric acid gives the weight of mixed iron and aluminium oxides, and deduction of the iron oxide from this gives aluminium oxide by difference.

Acetate Method.[1] The acetate method, which gives identical results, is carried out as follows:—

Two g. of phosphate is treated with strong hydrochloric acid. The solution is evaporated to dryness and the residue redissolved in acid and water and filtered from the siliceous residue. The filtrate is oxidised by addition of bromine water, nearly neutralised with ammonia, cooled and precipitated with excess of ammonium acetate solution containing an excess of acetic acid. After standing some hours, the precipitate is filtered off and washed with hot water.

The bulky precipitate contains all the iron and aluminium oxides (as phosphates), together with a varying quantity of calcium phosphate. It is dried, ignited and weighed. It is then dissolved in a very small quantity of hydrochloric acid and about 1 g. of citric acid and 0·5 g. of ammonium oxalate added, slight excess of ammonia, and then excess of acetic acid. After simmering gently for half an hour the calcium oxalate is filtered off, ignited at a low temperature and weighed as carbonate. The phosphoric acid is then determined, exactly as in the citric-oxalic-magnesium method of phosphate analysis described on p. 518, except that the operation is conducted all through in solutions of very small bulk. The sum of the lime and phosphoric acid deducted from the weight of the ammonium acetate precipitate gives the iron and aluminium oxides. The iron is determined in the total filtrates and washings from the precipitation and reprecipitation of the ammonium magnesium phosphate, being precipitated by ammonium sulphide, as already described in the modified Glaser method.

In the laboratory of the writer, both these methods are in constant use, being carried out simultaneously by different operators in duplicate analyses of the same sample, usually with very close concordance in the results.

Direct Determination of Aluminium Oxide—Lasne Method.[2] In both the foregoing processes aluminium oxide is taken by difference, and for commercial or technical purposes direct determination is rarely needed, but an accurate method has been elaborated by H. Lasne based upon the well-known solubility of aluminium phosphate in sodium hydroxide. His process is accurate but tedious, and involves careful observance of minute details.

[1] This method (as well as the foregoing modified Glaser method) is described by the writer in *Thorpe's Dict. of Applied Chemistry* (3rd ed., vol. iii., p. 186), from which it is here quoted by permission of the publishers.

[2] *Bull. Soc. Chim.*, 1896 (iii), 15, 118, 146, 237.

Five g. of phosphate is treated with hydrochloric acid, the solution being evaporated to dryness, taken up with 60 c.c. of 10 per cent. hydrochloric acid, and digested at about 100° for one hour. The solution is diluted to 500 c.c. and filtered, 125 c.c. being taken for the determination of alumina. Five g. of sodium hydroxide (free from silica and alumina) and 1 g. of sodium phosphate is dissolved in 20 c.c. of distilled water in a nickel basin. Into this solution the 125 c.c. of phosphate solution is poured with constant stirring, and kept for about an hour at a temperature of about 100°, with occasional stirring, preferably with a nickel spatula. The liquid is cooled and made up to 250 c.c. in a glass flask. The contents are filtered, and 200 c.c. of the filtrate (= 1 g. of the phosphate sample) mixed with 30 c.c. of a solution of ammonium chloride (125 g. per litre), sufficient hydrochloric acid being added to dissolve such precipitate as is formed. Ammonia is then added in very slight excess. After boiling for five minutes the precipitate is filtered off, washed slightly once with water, and redissolved through the filter into the original beaker with a little 10 per cent. hydrochloric acid, the filter being washed with water five or six times. The solution is treated with 3·5 c.c. of a solution of pure ammonium phosphate (10 g. per 100 c.c.) and ammonia added till a permanent precipitate is formed, and then sufficient dilute hydrochloric acid to redissolve the precipitate. The fluid is diluted to 250 c.c., when 10 c.c. of a solution of ammonium thiosulphate (15 g. per 100 c.c.) is poured in. After half an hour's boiling, five drops of a saturated solution of sodium acetate are added, and after five minutes' further boiling, the precipitate is filtered off and washed seven or eight times with water. The precipitate, which is granular and not gelatinous, is ignited to constant weight, and assumed to have the composition of pure aluminium orthophosphate. Its weight multiplied by 0·418 gives the aluminium oxide in 1 g. of the sample.

Carbon Dioxide in Raw Phosphates

For most purposes the determination of carbon dioxide by loss in Schrötter's apparatus is sufficiently accurate; more accurate determinations can be made volumetrically (*e.g.* by Lunge and Rittener's apparatus, p. 297) or in any convenient apparatus in which the evolved carbon dioxide is collected and weighed. A suitable apparatus is described under Clays, etc., p. 12.

Estimation of Fluorine in Raw Phosphates

The estimation of fluorine in minerals is one of the more difficult analytical determinations particularly in presence of carbonic acid, chlorine and organic substances. Von Grueber[1] regards M. Hauffe's

[1] *Methode zur Untersuchung der Kunstdüngemittel*, 1898, [II].

modified form of H. Offermann's method[1] as the most reliable; this depends on the conversion of the fluorine present into silicon fluoride, which is decomposed by water and the hydrofluosilicic acid formed titrated with normal potassium hydroxide.

The sample must be rendered anhydrous if accurate results are to be obtained. Raw phosphates must be dried at 150° to 170°, or gently ignited; superphosphates are weighed out into a small platinum dish, milk of lime added till the mixture is distinctly alkaline, the water evaporated off on the water-bath, and the residue dried and gently ignited. When cold, the residue is ground fine and transferred to a flask by means of a dry funnel; the funnel and dish are then repeatedly rinsed with finely powdered, ignited quartz.

The sulphuric acid to be used must, as nearly as possible, be pure monohydrate. Every part of the apparatus must be absolutely dry

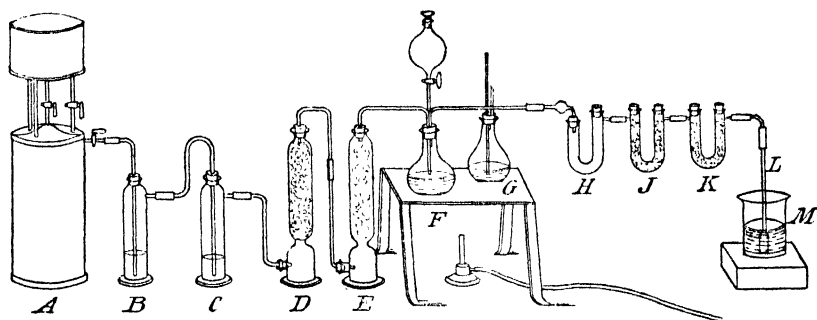



FIG. 85.

and the glass tubes must be in contact at the joints. The apparatus is arranged as follows (Fig. 85): A is an air gas-holder, but this may advantageously be replaced by a cylinder of compressed carbon dioxide fitted with a delicate "governor" tap. B is a wash-bottle containing an alkaline solution of potassium permanganate; from B the air passes through the wash-bottle C charged with concentrated sulphuric acid, and the absorption cylinders D and E filled respectively with granular soda-lime and small pieces of fused calcium chloride. If carbon dioxide, as is now suggested, be used instead of air from a gas-holder, soda-lime obviously cannot be used as a drying agent, and in that case the cylinders containing soda-lime may be replaced by an additional cylinder or wash-bottle of sulphuric acid. The flask F (capacity 300 to 400 c.c.) serves for the decomposition of the mineral; it is closed by a trebly bored stopper through which pass a separating funnel with a long stem and two glass tubes bent at right angles. The current of dry air enters by the longer of these two tubes, the shorter conducts away the mixture of air and silicon fluoride. The flask G is

[1] *Z. angew. Chem.*, 1890, 3, 615.

not connected to the apparatus; it contains as much concentrated sulphuric acid as is subsequently allowed to flow into F and is provided with a thermometer; this flask serves chiefly to determine and regulate the proper temperature for the decomposition.

The two flasks, F and G, are placed on an iron plate covered with wire gauze, in such a way that both are equally heated. The dry, empty U-tube H is connected on the one hand to the decomposition flask F, on the other hand to the tube J, filled with freshly fused calcium chloride, which must not have an alkaline reaction. The tube K contains pumice coated with anhydrous copper sulphate, and a little mercury is placed in the beaker M. A 15 or 20 c.c. pipette, L, cut through the middle and firmly clamped in a retort stand, serves as the delivery tube; the edges must be ground as smoothly as possible after cutting, and this wider end of the tube is dipped 1 or 1·5 mm. deep in the mercury.

The whole apparatus is first tested to make sure it is air-tight. The prepared substance is then placed in the flask F, together with fifteen to twenty times its weight of ignited quartz powder or finely powdered sand; if sand is used it must be purified by treatment with concentrated sulphuric and then hydrochloric acid, and thoroughly washed and ignited. The substance and quartz are mixed by shaking round, and the flask is placed in position; the beaker M is then filled with water (from 50 to 200 c.c.), the amount being adapted to the probable content of fluorine. An aqueous extract of quillaia is then added, made by boiling 1 g. of quillaia in 100 c.c. of water; twelve to sixteen drops of this extract are added to every 100 c.c. of water in the beaker. This provision causes the formation of a slight film of foam on the surface of the water when air is bubbled through, and thus ensures that the largest air bubbles give up the whole of their silicon fluoride to the water in M before bursting.

A current of air is then passed through the apparatus, and 50 to 60 c.c. of pure cold concentrated sulphuric acid is allowed to flow into the flask F from the separating funnel; the flask is then slowly heated to 150° to 155°, and when decomposition is complete, is allowed to cool, air being passed through the whole apparatus for another hour. The contents of the beaker M are then titrated while hot with $N/1$ or $N/2$ potassium hydroxide, litmus or phenolphthalein being used as indicator.

To make sure that the whole of the silicon fluoride has been driven out of the apparatus, the tube L may be replaced by a fresh one, and air conducted through the apparatus, with fresh water in M, for another half hour; the second portion of water is then titrated. One c.c. $N/1$ KOH = 0·019 g. F.

In America the method has been somewhat modified in detail,

chiefly with a view to determining small quantities of fluorides in such articles as baking powder.[1] The apparatus as there recommended includes absorption tubes or vessels containing solutions of silver sulphate and chromic acid respectively in anhydrous sulphuric acid. The accompanying figure shows the modified apparatus which is built up as follows:—

A is a source of gas (air, carbon-dioxide or nitrogen) which can be delivered under constant pressure; B, B are two wash-bottles containing concentrated sulphuric acid for washing the gas from A; C is a 100 c.c. flask from which the anhydrous sulphuric acid is introduced into the digestion flask; D is a 4 oz. Pyrex distilling flask into which a weighed quantity of the sample is introduced, together with quartz flour and 5 g. of anhydrous copper sulphate. The flask is provided with a small trap and reflux tube at its outlet; E is a Schmidt tube containing glass beads in one arm and in the other 10 c.c. of a silver sulphate

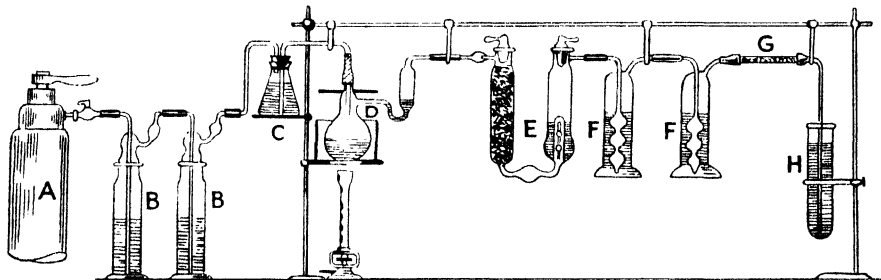



Fig. 86.

solution in anhydrous sulphuric acid which is prepared by dissolving 10 g. of silver sulphate (previously ignited with an excess of concentrated sulphuric acid to drive off any volatile acids) in 100 c.c. of concentrated sulphuric acid; F, F are two Bowen bulbs, each containing 25 c.c. of a saturated solution of chromic acid in anhydrous sulphuric acid; G is a glass tube ($6'' \times \frac{3}{8}''$) filled with glass wool (which wool, as well as the glass beads in E, should have been previously digested in strong hydrochloric acid, washed free from acid and dried); and H is a glass receiver containing water which may be either a capacious test tube (as shown in the illustration) or a beaker of convenient size.

The writer prefers to add the sulphuric acid to the digestion flask by means of a separating funnel, as indicated in the figure descriptive of the earlier apparatus, rather than transfer it by pressure from another flask, as in the American apparatus. The reason for this is that it is desirable to run a current of gas through the apparatus for some little time before the addition of the acid, in order to ensure as far as possible dryness of all its parts. With the acid originally *in situ*

[1] *Off. Methods of Anal. Assoc. Agric. Chem.*, 1925, pp. 312-314.

it is necessarily driven over into the digestion flask directly the current of gas is started so that if a gas current is to be preliminarily passed, this flask must at first be freed from acid and must then be opened in order to pour acid into it. Alternatively the acid might be introduced into C by a stoppered separating funnel after preliminary passage of gas. This is, however, merely a question of detail of manipulation.

The writer has further found it necessary, in some materials at any rate, to insert in the circuit a second Schmidt tube E containing sulphuric acid solution of silver sulphate in order to be quite sure of trapping any hydrochloric acid that may be evolved.

Whichever method be used, it is important that after the hydrofluosilicic acid has been titrated with sodium or potassium hydroxide solution (free from sulphates), the distillate, after reacidification, should be tested for traces of sulphuric acid that may have been carried over during the process, and if any is discovered it must be estimated and allowed for in calculating the result.

In the account given[1] where small quantities of fluorine only are under consideration, it is recommended that the percentage of fluorine calculated from the analysis should be multiplied by the factor 1·11 to compensate for the average experimental error based upon experience of the method. So large a correction, however, is scarcely applicable to the larger quantities of fluorine found in raw mineral phosphates though it might well be applicable to the much smaller quantities found in superphosphate made therefrom.

III.—POTASH

The determination of potash may be conveniently considered under two heads; first, potash in commercial potash salts, viz., "sulphate of potash," "muriate of potash," "nitrate of potash," and the large range of saline mixtures, such as kainit, hard-salz, etc., either in their "native" forms or altered or adjusted by concentration or admixture; secondly, we have to consider the determination of potash in guano or in other natural or artificially compounded fertilisers in which potash salts form an ingredient.

The analysis of potassium salts generally used is dealt with in detail in the section on that subject in Vol. II. (pp. 399-427), and consequently only special details are here considered. The potash obtained from either of the classes of materials mentioned above is finally weighed either as potassium platinum chloride or as potassium perchlorate. The latter method has come into very extensive use

[1] *Loc. cit.*

owing to the greatly increased cost of platinum chloride since the earlier days when no other satisfactory method was available.

It is not necessary to discuss the modifications of the platinum process that have been recommended, and it will be sufficient to quote the present official regulations.

The perchlorate method is based upon the insolubility of potassium perchlorate in alcohol. This comparative insolubility, however, is sufficiently incomplete to have been a source of variable error in the process first devised, but the method has now been reduced to an accuracy comparable with that of the platinum method by using, in the final washing of the precipitate, alcohol already saturated with potassium perchlorate.[1]

To the process now in use, which is set forth in the official regulations on p. 551, the following prefatory remarks may be made. First as to commercial potash salts containing sulphates, as is usually the case. Prior to the determination of the potash, sulphuric acid must be removed by precipitation with barium chloride. The official regulations merely prescribe that barium chloride solution should be added drop by drop to the boiling acid solution of the salts until the sulphuric acid is completely precipitated. If the quantity of sulphuric acid in the solution is not already known, its exact precipitation is a little tedious. If the mark is overshot, the excess of barium thus accidentally added must in turn be precipitated by the addition of diluted sulphuric acid until by trial and error there is excess of neither barium nor sulphuric acid. The writer finds it more convenient to determine preliminarily the exact quantity of sulphuric acid in the material under investigation and then add to the solution a quantity of barium chloride exactly equivalent to the sulphuric acid.

In guanos or mixed fertilisers two methods are given for the sufficient removal of interfering substances before the determination of the potash. The first is the precipitation of a hydrochloric acid solution of the incinerated fertiliser with barium hydroxide and the subsequent precipitation of the filtrate with ammonium hydroxide and ammonium carbonate with the addition of a little ammonium oxalate, the filtrate being evaporated to dryness and the ammonium salts expelled by gentle heat. This is the method commonly in use. The alternative method, of which the present writer has no personal experience but which is largely used in some agricultural laboratories, is based upon preliminary precipitation of the potash from the hydrochloric acid solution of the incinerated fertiliser by the use of sodium cobaltinitrite. The precipitate is dissolved in hydrochloric acid and the potash therein determined as perchlorate.

[1] For a detailed discussion see W. A. Davies, *J. Agric. Sci.*, 1912, 1, 52; and R. L. Morris, *Analyst*, 1920, 45, 349.

Details of the methods are given in the following official regulations of the Ministry of Agriculture.[1]

Determination of potash.—Potash shall be determined by the perchloric acid method or, alternatively, by the platinum chloride method.

(1) *Perchloric acid method.*

(a) *Salts of potash free from sulphates.* A weighed portion of the sample equivalent in potash content to 1·5 to 2·0 g. of potash (K_2O) shall be dissolved in water. The solution shall be filtered if necessary and made up to 500 millilitres. The potash shall be determined in 50 millilitres of the solution by precipitation with perchloric acid as described in paragraph (v) (1) (d).

(b) *Salts of potash containing sulphates.*

(A) A weighed portion of the sample equivalent in potash content to 1·5 to 2·0 g. of potash (K_2O) shall be boiled with 300 millilitres of water to which 20 millilitres of hydrochloric acid have been added. Barium chloride solution shall be cautiously added, drop by drop, to the boiling solution until the sulphuric acid is completely precipitated. The liquid shall be cooled, made up to 500 millilitres and filtered. 50 millilitres of the filtrate shall be taken and evaporated to dryness and shall then be moistened with concentrated hydrochloric acid, again evaporated to dryness, treated with a little dilute hydrochloric acid and filtered if necessary. The potash shall be determined by precipitation with perchloric acid as prescribed in paragraph (v) (1) (d).

If the solution contains phosphates, iron, manganese or other substances that would interfere with the determination of potash, the method prescribed in paragraph (v) (1) (c) is to be used instead of the method prescribed in paragraph (v) (1) (b).

(B) *Alternative method.* A weighed portion of the sample equivalent in potash content to 1·5 to 2·0 g. of potash (K_2O) shall be boiled with 300 millilitres of water, cooled, made up to 500 millilitres and filtered. To 50 millilitres of the filtrate, 30 millilitres of a solution of sodium cobaltinitrite shall be added, the mixture stirred and allowed to stand for not less than two hours. It shall then be filtered and washed with water containing a small amount of the cobaltinitrite solution.

[1] *Fertilisers and Feeding-Stuffs Regulations*, 23rd May 1928.

The precipitate shall be dissolved in hot dilute hydrochloric acid and the solution filtered into a small porcelain dish and evaporated to dryness. The residue shall be dissolved in water and the potash determined by precipitation with perchloric acid as prescribed in paragraph (v) (1) (d).

(c) *Potash in guanos and mixed fertilisers.*

(A) Ten g. of the sample shall be gently incinerated in order to char organic matter, if present, and shall then be heated for ten minutes with 10 millilitres of concentrated hydrochloric acid and finally boiled with 300 millilitres of water. The liquid shall be filtered, raised to the boiling point and powdered barium hydroxide shall be added until slightly alkaline. It shall then be cooled, made up to 500 millilitres and filtered. Of the filtrate, 250 millilitres shall be treated with ammonia solution and excess of ammonium carbonate and then, while boiling, with a little powdered ammonium oxalate, cooled, made up to 500 millilitres and filtered. Of the filtrate, 100 millilitres are to be evaporated in a porcelain dish to dryness. If desired, nitric acid may be added during the evaporation after free ammonia has been driven off. The residue is to be heated gently over a low flame till all ammonium salts are expelled, the temperature being carefully kept below that of low redness. The residue shall be moistened with concentrated hydrochloric acid, evaporated to dryness, treated with dilute hydrochloric acid and filtered. The potash shall be determined in the filtrate by precipitation with perchloric acid as prescribed in paragraph (v) (1) (d).

(B) *Alternative method.*

Ten g. of the sample shall be gently incinerated in order to char organic matter, if present, and shall then be heated for ten minutes with 10 millilitres of concentrated hydrochloric acid and finally boiled with 300 millilitres of water. The liquid shall be filtered into a half-litre flask and the residue washed. The solution shall be made up to 500 millilitres and 50 millilitres taken, boiled with solution of sodium nitrite to expel ammonium salts, if present, and evaporated to dryness. The residue shall be dissolved in water containing a little hydrochloric acid and sufficient sodium citrate added to prevent precipitation of phosphates. It shall then be mixed with 30 millilitres of cobaltinitrite solution, in the manner described in paragraph (v) (1) (b) (B) and the precipitate treated as therein directed.

(d) *Precipitation of potash as potassium perchlorate.* To the solution obtained as above described in paragraphs (v) (1) (a), (b) or (c) and placed in a small glass or porcelain basin, about 7 millilitres of a 20 per cent. solution of perchloric acid (sp. gr. 1·125), free from chloric acid, shall be added. The basin shall be placed on a hot plate or sand bath and the contents evaporated until white fumes are copiously evolved.

The precipitate shall be redissolved in hot water, a few drops of perchloric acid solution added and the whole concentrated again to the fuming stage. After cooling, the residue in the basin shall be thoroughly stirred with 20 millilitres of alcohol of sp. gr. 0·816 to 0·812 (95 to 96 per cent. of alcohol by volume). The precipitate shall be allowed to settle and the clear liquid shall be poured through a weighed or counterpoised filter paper, or through a Gooch crucible, draining the precipitate as completely as possible from the liquid before adding the washing solution. The precipitate shall be washed by decantation with alcohol (as above) saturated with potassium perchlorate at the temperature at which it is used, pouring the washings through the paper or Gooch crucible on which the whole of the precipitate is finally collected, dried at 100° C. and weighed. The precipitate is to be regarded as $KClO_4$ and is to be calculated to its equivalent as K_2O.

(e) *Preparation of the cobaltinitrite solution.* The cobaltinitrite solution shall be prepared as follows:—Fifty g. of cobalt nitrate and 300 g. of sodium nitrite shall be dissolved in water, acidified with 25 millilitres of glacial acetic acid and diluted to a litre. The solution shall be filtered after standing twenty-four hours and is then ready for use. It must be kept in the dark.

(2) *Platinum chloride method.*

(a) *Salts of potash free from sulphates.* A weighed portion of the sample equivalent in potash content to 1·5 to 2·0 g. of potash (K_2O) shall be dissolved in water; the solution shall be filtered if necessary and made up to 500 millilitres. The potash shall be determined in 50 millilitres of the solution by the platinum chloride method prescribed in paragraph (v) (2) (d).

(b) *Salts of potash containing sulphates.* A weighed portion of the sample equivalent in potash content to 1·5 to 2·0 g. of potash (K_2O) shall be boiled with 300 millilitres of water to

which 20 millilitres of hydrochloric acid have been added. Barium chloride solution shall be cautiously added, drop by drop, to the boiling solution until the sulphuric acid is completely precipitated. Any slight excess of barium shall be removed by the addition of the least possible excess of dilute sulphuric acid. The liquid shall be cooled, made up to 500 millilitres and filtered. Fifty millilitres of the filtrate shall be taken and evaporated to dryness and shall then be moistened with concentrated hydrochloric acid, again evaporated to dryness, treated with a little dilute hydrochloric acid and filtered if necessary. The potash shall be determined in the filtrate by the platinum chloride method, prescribed in paragraph (v) (2) (d).

If the solution contains phosphates, iron, manganese, magnesium or other substances that would interfere with the determination of potash, the method prescribed in paragraph (v) (2) (c) is to be used instead of the method prescribed in paragraph (v) (2) (b).

(c) *Potash in guanos and mixed fertilisers.* Ten g. of the sample shall be gently incinerated in order to char organic matter, if present, and shall then be heated for ten minutes with 10 millilitres of concentrated hydrochloric acid and finally boiled with 300 millilitres of water. The liquid shall be filtered, raised to the boiling point and powdered barium hydroxide shall be added until slightly alkaline. It shall then be cooled, made up to 500 millilitres and filtered. Of the filtrate, 250 millilitres shall be treated with ammonia solution and excess of ammonium carbonate and then, while boiling, with a little powdered ammonium oxalate, cooled, made up to 500 millilitres and filtered. Of the filtrate, 100 millilitres are to be evaporated in a porcelain dish to dryness. If desired, nitric acid may be added during the evaporation after free ammonia has been driven off. The residue is to be heated gently over a low flame till all ammonium salts are expelled, the temperature being carefully kept below that of low redness. The residue shall be moistened with concentrated hydrochloric acid, evaporated to dryness, treated with dilute hydrochloric acid and filtered. The potash shall be determined in the filtrate by the platinum chloride method prescribed in paragraph (v) (2) (d).

(d) *Precipitation of potash as potassium chloroplatinate.* To the solution obtained as above described in paragraphs (v) (2) (a), (b) or (c), a few drops of hydrochloric acid shall be

added, if none is present, and also 10 millilitres or an excess of solution of platinum chloride containing 10 g. of platinum per 100 millilitres. After evaporation to a syrupy consistency on a water-bath, the contents of the basin shall be allowed to cool and shall then be treated with alcohol of sp. gr. 0·864, being washed by decantation until the alcohol is colourless. The washings shall be passed through a weighed or counterpoised filter paper, on which the precipitate shall be finally collected, washed with alcohol as above, dried at 100° C. and weighed. The precipitate is to be regarded as K_2PtCl_6 and is to be calculated to its equivalent as K_2O.

IV.—FINENESS OF MATERIALS

Basic slag and finely ground raw mineral phosphates are sold with guarantees of percentage of "fine meal" or "fineness."

The Ministry of Agriculture (1928) has accordingly made the following prescription as to the sieve to be used and the manner in which it should be used.

(ix) *The prescribed sieve.*

(*a*) The sieve[1] to be used for the purpose of the statement as to fineness of grinding of basic slag, ground limestone and raw phosphate or phosphate rock shall be of the following dimensions:—The standard diameter of the wire and the standard length of the side of the aperture shall be each 0·141 mm.; no wire shall anywhere be less than 0·137 mm. in diameter, and no aperture shall be greater than 0·155 mm. in length of side.

(*b*) The sieving of a sample shall be carried out as follows:— Twenty g. of the sample shall be dried at 100° C. and then be transferred to the sieve with the lower receiver attached. The sieve shall then be shaken for ten minutes with occasional tapping of the sides of the sieve. At the end of ten minutes, the material which has passed through into the lower box shall be carefully brushed out into a suitable vessel and weighed. The receiver shall be replaced and the shaking repeated for another ten minutes, when the sifted matter shall again be removed, mixed with the first portion and weighed. The process shall be repeated until not more than 0·2 per cent. is sifted during ten minutes.

[1] The apertures of the prescribed sieve are practically identical with those of the 90 I.M.M. (Institution of Mining and Metallurgy) sieve and also of the Amandus Kahl 100 E sieve.

> Soft lumps which can be caused to crumble by application of the fibres of a bristle brush shall be broken down after each shaking period, but in such manner that the hard parts of the brush do not come into contact with the sieve. The brush shall not be used in any way to brush particles through the sieve.

Some confusion and annoyance has been caused owing to the different gauges of wire used by different makers of gauze having the same number of meshes per linear inch or per square inch, owing to which differences the 100 mesh (or 10,000 mesh) gauze of one maker has apertures of a larger size than the similarly described gauze of another maker. The mere statement that a given powder gave 80 per cent. of "fine meal" when sifted through a sieve of 10,000 apertures per square inch may be misleading, as two operators, having sieves of different makes both complying with this numerical specification, may obtain materially different results. This was long ago recognised in connection with basic slag, which was formerly the only fertiliser sold on a "fine meal" basis, and on the suggestion of Wagner led to the practically universal adoption (for testing basic slag) of a sieve of gauze known as 100 E, made by Amandus Kahl of Hamburg. The sieve now prescribed by the Ministry of Agriculture, viz., the 90 I.M.M. (Institution of Mining and Metallurgy) sieve, has apertures nearly identical with what are supposed to be the dimensions of the German gauze mentioned. But different batches of gauze made to the same specification, even though the wire may be of regular gauge and the number of meshes per inch identical, may vary in the regularity of the weaving. A little difference between the widths of the spaces between adjacent wires here and there in the same sieve may make a considerable difference in the sifting results, even between two sieves made from the same stock piece of gauze, and the writer has recently found considerable variations in the results given by different sieves made from the same I.M.M. specification. This applies not only to the 90 I.M.M. sieve but to the Amandus Kahl gauge.

If the conditions laid down by the Ministry could be accurately controlled—for example, that where the standard length of the side of the apertures should be each 0·141 mm., no aperture anywhere should have a greater width than 0·155 mm., a more satisfactory degree of uniformity might be obtainable; but this requirement appears to be difficultly realisable. Consequently, determination of "fineness" or of "fine meal" must be viewed with latitude.

The present regulations of the Ministry of Agriculture, under the Fertilisers and Feeding Stuffs Act, require that when the vendor of

slag gives a statement of fineness as, for example, 80 per cent., the limit of variation allowed should be 1/20th of the amount stated, viz., in this case 4 per cent.; but in view of what has been said it is evident that the grinder of the material will be wise if he provides a larger percentage of "fine meal" than the minimum which he prepared is to guarantee, as the latitude officially allowed does not appear to err on the liberal side.

The difficulties mentioned, while applicable to the sieve of officially prescribed dimensions, apply in a greater degree to the finer sieves of 100 or even 120 meshes per linear inch, by which the grinders of raw mineral phosphates now frequently elect to have their materials tested. They are not bound by official regulations to do more than guarantee fineness through the prescribed 90 I.M.M. sieve, but competition appears to induce them to give a higher guarantee. Although, however, this guarantee of greater fineness is from the legal point of view optional, it nevertheless becomes legally binding if given. It is in connection with these higher degrees of fineness that the variations between different makes of gauze having a like number of meshes per inch, or even between different pieces of the same make, seem to call for a little more latitude than that laid down in the regulations in relation to the prescribed sieve.

Lime, Chalk, Ground Limestone, Slaked Lime, Etc.

These materials, used in application to the land from time immemorial, have only lately been officially recognised as "fertilisers," as to the composition of which the vendors are expected to furnish information to purchasers under the provisions of the Fertilisers and Feeding Stuffs Act (1928).

To determine total calcium, a suitable quantity of the material, say 2 g., is dissolved in hydrochloric acid, the solution in the case of burnt or slaked lime being evaporated to dryness to render the silica insoluble. The silica is filtered off and the total lime determined as already described under calcium sulphate. The calcium carbonate is arrived at by determining the carbon dioxide by any convenient method (*cf.* p. 545). Under the present regulations of the Ministry of Agriculture special regulations are laid down for the determination of lime in burnt lime and slaked lime with a view to expressing the available lime in an alkaline form as distinguished from that present as calcium carbonate and as calcium silicate. Directions are included for the determination of calcium carbonate in ground chalk, ground limestone or dried calcium carbonate. These are as follows:—

(vii) *Determination of lime in burnt lime and in calcium hydroxide (hydrated lime).* A portion of the sample shall be

rapidly ground and passed through a sieve having apertures about 0·2 mm. square, and from this specially prepared portion the quantities for determination of lime shall be weighed.

A quantity of the sample about 5 g. in weight, accurately weighed, shall be transferred to a stoppered bottle of about 1 litre capacity and moistened with 10 millilitres of alcohol neutral to phenolphthalein, to lessen the possibility of caking. 490 millilitres of a 10 per cent. solution of cane sugar (made neutral to phenolphthalein) shall be added and the bottle at once fitted into a shaking apparatus and agitated for a period of not less than four hours. The solution shall then be filtered through a dry paper into a dry vessel and 50 millilitres of the filtrate shall be titrated with seminormal hydrochloric acid (HCl) using phenolphthalein as indicator.

The method gives the total amount of lime present in the sample in the form of caustic lime (CaO) and of calcium hydroxide ($Ca(HO)_2$) and the result may be calculated to CaO, or $Ca(HO)_2$ as desired.

(viii) *Determination of calcium carbonate in ground chalk, ground limestone and dried carbonate of lime.*

(*a*) A weighed quantity of the finely ground sample shall be treated with dilute hydrochloric acid until effervescence ceases, the solution filtered and the insoluble matter washed. The calcium shall be precipitated from the filtrate as oxalate and weighed as oxide. Steps shall be taken to exclude from the oxalate precipitate iron, alumina and other interfering substances.

(*b*) The amount of carbon dioxide evolved on treatment of a weighed quantity of the finely ground sample with dilute acid shall be determined in a suitable apparatus.

(*c*) The amount of calcium oxide determined under (*a*) shall be calculated to calcium carbonate, provided that the necessary equivalent of carbon dioxide is present in the sample. If less than the equivalent of carbon dioxide is present in the sample the quantity of carbon dioxide determined under (*b*) shall be calculated to calcium carbonate.

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FEEDING STUFFS

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I. EXAMINATION OF CONCENTRATED FEEDING STUFFS

Sampling.—Sampling of oil cakes and meals is commonly conducted by cargo superintendents or professional samplers in well-understood conventional fashion, but for the purpose of the Fertilisers and Feeding Stuffs Act (1926) the manner of taking samples has been definitely prescribed by the Ministry of Agriculture[1] in the following terms:[2]—

In the Case of a Feeding Stuff—

(vii) When the feeding stuff is in the state of small lumps or meal, it shall be sampled in the same manner as prescribed for fertilisers under paragraphs (i), (ii) and (iii). (See p. 491.)

(viii) When the feeding stuff is in the state of cake, a number of cakes shall be selected from different parts of the whole quantity as follows:—

	Cakes.
Where the quantity does not exceed 2 tons	5
Where the quantity exceeds 2 tons and does not exceed 5 tons	10
Where the quantity exceeds 5 tons and does not exceed 50 tons	15
Where the quantity exceeds 50 tons and does not exceed 100 tons	25

In each case the quantity shall be treated as composed of separate approximately equal portions, the number of portions being reckoned as the same as the number of cakes to be selected for the purpose of sampling, and one cake shall be drawn by the inspector or official sampler at random from each of these portions.

Where the quantity exceeds 50 tons it may, in the discretion of the inspector or official sampler, be treated as composed of separate parcels of 50 tons each, any one of which may be sampled separately; but where two or more samples are taken under this provision from one quantity, they shall be mixed together to form one sample for the purposes of the Act.

[1] *Fertilisers and Feeding Stuffs Regulations*, 23rd May 1928.

[2] The Roman numerals and small letters in brackets are retained to facilitate reference to the Regulations.

(ix) The selected cakes shall be broken by a cake-breaker or in some other manner so that the whole shall pass through a sieve with meshes one and a quarter inch square. The broken pieces shall then be thoroughly mixed, and from the mixture a sample of not less than 6 lb. in weight shall be taken.

(x) Where any appreciable portion of the feeding stuff appears to be mouldy or is otherwise apparently unsuitable for feeding purposes, separate samples shall be taken of the unsuitable portion and of the residue of the feeding stuff respectively, and in the case of unsuitable cakes, the sample may consist of several large pieces representative thereof.

(xi) When the feeding stuff is in a fluid or semi-fluid condition, packages shall be taken at random in accordance with the scale shown in paragraph (i) (p. 491), the contents well mixed by stirring or shaking, and a similar quantity taken from each. These portions shall then be mixed together, in a clean dry vessel, and from the mixture a sample of from 2 lb. to 4 lb. in weight shall be taken.

(xii) Where the quantity of the whole consignment does not exceed 2 cwts., the sample may consist of such a portion of the consignment or bulk as is fairly representative of the whole, and the sample shall be of such a quantity that each of the parts into which (under paragraph D) it is to be divided will be not less than half a pound in weight.

Preparation of Sample. The preparation of the sample for analysis is officially prescribed as follows:—

(a) If the sample is in a fine condition and passes through a sieve having apertures about 1 mm. square, it shall be thoroughly mixed and a portion not less than 100 g. in weight shall be placed in a stoppered bottle. From this portion the quantities for analysis shall be taken.

(b) If the sample does not wholly pass through a sieve having apertures about 1 mm. square and wholly passes through a sieve having apertures from 2 to 3 mm. square, it shall be thoroughly mixed and a portion for the determination of the moisture shall be at once taken.

(c) If the sample is in a coarse condition, as, for example, pieces of broken cake, it shall be carefully pulverised until the whole passes through a sieve having apertures from 2 to 3 mm. square. It shall then be thoroughly mixed and a portion for the determination of the moisture shall be at once taken.

(d) From the mixed sample as under (b) above, or from the coarsely crushed sample as prepared under (c) above, a portion not

less than 100 g. in weight shall be taken and further powdered and passed through a sieve having apertures about 1 mm. square. The portion of the sample so prepared shall be placed in a stoppered bottle and from it the quantities for analysis shall be weighed.

(e) If the original sample is appreciably moist, or if for any reason the operations of pulverisation and mixing are likely to result in loss or gain of moisture, the moisture shall be determined in this prepared portion, as well as in the sample prepared as in paragraph (i) (b) or (c) in order that the results of the analysis may be corrected to correspond with the sample in its original condition as regards moisture.

(f) Materials which cannot be conveniently pulverised or passed through a sieve shall be thoroughly mixed by the most suitable means.

In the conventional commercial analysis of feeding stuffs for agricultural purposes, the constituents usually stated are:—Moisture, oil or fat, albuminoids or proteins, digestible carbohydrates, fibre, ash, sand and other siliceous matter, and sometimes (as in meat and bone meal, or fish meal) phosphoric acid or its equivalent in tricalcium phosphate. Sugar also, as apart from other carbohydrates, has sometimes to be determined, as in what are known as "sugar feeds," and sometimes, also, starch.

Moisture is usually construed as the loss of weight on drying to constancy in a water-oven, or sometimes by more rapid drying at a temperature of 105° to 110°. In America the drying is carried out at 100° under a reduced pressure of 100 mm. of mercury, or at atmospheric pressure in a current of dry hydrogen—or alternatively by drying cold in a vacuum desiccator over sulphuric acid.

Oil or Fat is determined by extraction of a weighed quantity of the prepared feeding stuff with either petroleum spirit or ether in a Soxhlet apparatus or some equivalent apparatus for continuous extraction. Ether (ethylic ether made from methylated spirit and frequently spoken of as "methylated ether") has been in use in England up to the present year (1928) but has now been officially superseded by petroleum spirit. In some continental countries and in America ether is still in use, as recommended in the report of an International Committee for the analysis of Fertilisers and Feeding Stuffs and adopted at the International Congress of Applied Chemistry at Berlin in 1903. Extraction by petroleum spirit, however, gives a nearer approach to the true oil or fat, as many feeding stuffs contain, in addition to true fats, variable quantities of other substances extractable by ether. When ether is used, it must be washed free from alcohol

with water in a separator, and subsequently dried by shaking with calcium chloride or lime, and redistilled from dry lime. The dehydration may be completed by adding small pieces of metallic sodium until evolution of hydrogen ceases, as directed in American Methods of Analysis.[1]

Albuminoids (or Protein or Crude Protein, conventionally alternative terms) are estimated by multiplying the nitrogen content in the feeding stuffs by the factor 6·25. This is obviously an empirical factor since the total nitrogen may include nitrogen in such forms as amides while the various forms of true proteins contain variable proportions of nitrogen. These considerations are, however, ignored in practice. The nitrogen is determined as in Fertilisers (see p. 496 *et seq.*).

For special purposes it may be desired to discriminate between the nitrogen in true protein form and nitrogen present as amides, etc., in some feeding stuffs (see p. 571).

Fibre or Crude Fibre.—Fibre is the fat-free and ash-free residue left after successive treatment of the feeding stuffs with dilute acid and dilute alkali under conventionally standardised conditions, being intended to furnish some approximate indication of the percentage of indigestible matter. Actual digestion experiments have weakened the confidence once placed in the correctness of the supposition on which the laboratory determination of fibre was based, but the estimation is valuable for comparative purposes and forms part of the routine of agricultural analysis.

Ash is determined in the usual way by incineration at a moderate temperature, and **Sand or Siliceous Matter** is determined in the ash after moistening with hydrochloric acid, evaporation to dryness, and re-solution in hydrochloric acid.

Digestible Carbohydrates are usually taken by difference.

Further observations on some of the foregoing items of analysis will be added subsequently, but it is convenient to reproduce here the methods now officially prescribed in England by the Ministry of Agriculture for the more important of the foregoing determinations.[2]

OFFICIAL METHODS

(ii) *Determination of Moisture (Loss on Drying).* A weighed quantity of the sample shall be dried at 100° C.

(iii) *Determination of Oil*—

(a) A weighed quantity of the sample shall be placed in an extraction thimble, which shall then be placed in an extraction apparatus and extracted with petroleum spirit, boiling-point 40° to 60° C. At the end of three to four hours the thimble

[1] *Off. Methods of Anal. Amer. Assoc. Agric. Chem.*, 1925, p. 117.

[2] *Fertilisers and Feeding Stuffs Regulations*, 23rd May 1928.

shall be removed from the apparatus, dried and its contents finely ground, preferably with sand, in a small mortar previously rinsed with petroleum spirit. The substance shall then be returned to the thimble, the mortar being washed out with petroleum spirit and the extraction continued for another hour. The extract should be free from suspended matter. After evaporation of the solvent, the oil shall be dried at 100° C. and weighed.

(b) In the case of samples containing saccharine matter, the weighed portion in the thimble shall be washed with water and then dried, previous to the extraction.

(iv) *Determination of Albuminoids (Protein).* The percentage of albuminoids (protein) shall be ascertained by multiplying the percentage of nitrogen, other than nitrogen present as ammoniacal or nitric nitrogen, by 6·25. The presence of nitrogen in these latter forms shall be tested for and the quantity so present, if any, shall be determined and deducted from the total nitrogen. (See methods for determination of ammoniacal nitrogen and nitric nitrogen in presence of organic matter under Methods of Analysis of Fertilisers, paragraph (iii), pp. 503, 506.)

The determination of total nitrogen in the absence of nitrates shall be as follows:—

A weighed portion of the sample shall be transferred to a Kjeldahl digestion flask, 25 millilitres of concentrated sulphuric acid (or more if necessary) shall be added and the flask gently heated until frothing ceases. Ten g. of potassium or sodium sulphate (anhydrous) shall then be added and the flask further heated until the colour of the clear liquid ceases to diminish. The heating shall be continued for an hour thereafter to ensure complete oxidation of the organic matter. The operation may be accelerated by the addition of a small crystal of copper sulphate or a globule of mercury to the liquid in the digestion flask.

The quantity of ammonia present in the liquid shall be determined by distillation into standard acid after liberation with alkali, and where mercury has been used, with the addition also of sodium or potassium sulphide solution.

The materials used shall be examined as to their freedom from nitrogen by means of a control experiment carried out under similar conditions with the same quantities of the reagents which have been employed in the actual analysis, One g. of pure sugar being used in place of the weighed portion of the sample. The quantity of standard acid found to have

been neutralised in this control experiment shall be deducted from the total quantity of acid neutralised in the distillation of the sample.

If nitrates are present, the digestion and subsequent distillation must be carried out as in Methods of Analysis of Fertilisers, paragraph (iii) (b) (p. 503).

(v) *Determination of Phosphoric Acid.* A weighed portion of the sample shall be heated with concentrated sulphuric acid until all organic matter is destroyed and the phosphoric acid is completely in solution. After dilution, the solution shall be filtered, the insoluble matter thoroughly washed and the filtrate made up to a definite bulk. The phosphoric acid shall be determined by the method prescribed in Methods of Analysis of Fertilisers, paragraph (iv) (d), in an aliquot part of the solution, which shall first be nearly neutralised and then acidified with nitric acid.

(vi) *Determination of Fibre.* Two or three g., accurately weighed, shall be extracted with petroleum spirit, boiling-point 40° to 60° C., in an extraction apparatus, or at least three times by stirring, settling and decantation, and the dry residue transferred to a conical 1000 millilitre flask. The material must not be further ground during extraction. A volume of 200 millilitres (c.c.) of a solution containing 1·25 g. of sulphuric acid (H_2SO_4) per 100 millilitres measured at ordinary temperature and brought to boiling-point, shall be added to the flask and heated. The contents of the flask must come to boiling within one minute and the boiling throughout must be gentle and continuous for exactly thirty minutes, the original volume being maintained. The flask shall be rotated every few minutes in order to mix the contents and remove particles from the sides. At the end of thirty minutes the flask shall be removed and the contents poured at once into the shallow layer of hot water remaining in a funnel fitted with a pump-plate or alternatively into the similar layer remaining in a Buchner funnel. The funnel shall be prepared by cutting a piece of cotton cloth or filter paper to cover the holes, so as to serve as a support for a disc of ordinary filter paper; boiling water shall be poured into the funnel and allowed to remain until the funnel is hot, whereupon suction is applied. The experiment shall be discarded if the time of filtration of the bulk of the 200 millilitres exceeds ten minutes. The residue shall be washed with boiling water until the washings are free from acid. The residue shall then be washed from the filter paper back into the flask with a volume of 200 millilitres of a solution of sodium hydroxide,

containing 1·25 g. of sodium hydroxide (NaOH) per 100 millilitres free or nearly free from sodium carbonate, measured at ordinary temperature and brought to boiling-point. The contents of the flask shall be boiled for exactly thirty minutes, the precautions given for the treatment with acid being observed. At the end of thirty minutes the flask shall be removed and its contents immediately filtered through an ordinary filter paper. The residue collected on the filter paper shall be washed with boiling water, then with a solution of 1 per cent. hydrochloric acid and again with boiling water until free from acid. The residue shall then be washed twice with 95 per cent. alcohol and three times with ether. The residue shall then be transferred to a dried weighed ashless filter paper, dried at about 100° C. in an oven and weighed in its weighing bottle until constant in weight. The ash of the paper and contents shall be determined by incineration at a dull red heat. The weight of ash shall be subtracted from the increase of weight found on the paper and the difference shall be reported as fibre.

(vii) *Determination of Sugar.*—

(a) *When the substance is in solid form.*—About 10 g. of the sample or a larger quantity if the percentage of sugar is low, accurately weighed, shall be ground up with water in a mortar and transferred to a 250 millilitre flask, using in all about 200 millilitres of cold water. The flask shall be shaken at intervals during 30 minutes. If it is necessary to use a clearing agent, basic lead acetate solution followed by sodium sulphate, or alumina cream free from ammonia, shall be employed. The liquid in the flask shall then be made up to 250 millilitres and filtered. The sugar shall be determined in 50 millilitres of the filtrate by the method prescribed in paragraph (vii) (c).

(b) *When the substance is in liquid form.*—The prepared portion of the sample shall be thoroughly mixed immediately before weighing out the quantity for sugar determination. About 10 g. of the sample, accurately weighed, shall be washed into a 250 millilitre flask with about 200 millilitres of water and the solution cleared, if necessary, with basic lead acetate solution followed by sodium sulphate, or alumina cream free from ammonia. The liquid in the flask shall then be made up to 250 millilitres and filtered. The sugar shall be determined in 25 millilitres of the filtrate by the method prescribed in paragraph (vii) (c).

(c) The aliquot part of the filtrate obtained as described in paragraph (vii) (a) or (b) shall be measured into a 100 millilitre flask and the sugar inverted as follows: 5 millilitres of hydrochloric acid of 38·3 per cent. strength shall be added and the flask placed in a water-bath maintained at 70° C. The solution in the flask should reach a temperature of 67° to 69° C. in 2½ to 3 minutes. It is maintained at 69° C. for 7 to 7½ minutes, the total period of heating being 10 minutes. It is then cooled at once, neutralised, bulked to 100 millilitres and filtered.

The total reducing sugar in the filtrate is determined either by gravimetric or volumetric process, the total copper-reducing power being calculated in terms of cane-sugar ($C_{12}H_{22}O_{11}$).

(viii) *Determination of Salt in Fish Meal.* Five g. of the sample shall be mixed with pure lime and heated until the organic matter is completely charred. The residue shall be extracted with water, the volume made up to 250 millilitres and the solution filtered. The chlorine shall be determined in an aliquot portion of the filtrate and the result expressed in terms of NaCl.

(ix) *Determination of Sand, Siliceous Matter or Other Insoluble Mineral Matter*—

(a) A weighed quantity of the sample, from 2 to 5 g., shall be incinerated and the weight of the ash shall be taken.

(b) The ash shall be moistened with hydrochloric acid and evaporated to dryness and shall then be repeatedly extracted with hot dilute hydrochloric acid (one part of concentrated hydrochloric acid to four parts of water). The solution shall be filtered and the insoluble matter washed, incinerated and weighed. The quantity obtained shall be taken as sand and siliceous matter.

(c) Where the quantity of sand and silica-free ash is so high as to raise a presumption that mineral material has been added, the nature and quantity of such added substances shall, if possible, be determined.

The foregoing regulations are binding upon English Agricultural Analysts for official work but, as has been already indicated (p. 562) in the preliminary observations relating to oil or fat extraction, they are not wholly in accord with the methods used in other countries. At the International Congress of Applied Chemistry held in Berlin, 1903, a code of directions was drawn up for international adoption. Although some of the methods therein prescribed have been re-discussed at subsequent International Conferences, no material alteration appears to have been made. The directions are here reproduced for reference.

METHODS FOR THE EXAMINATION OF FEEDING STUFFS IN INTERNATIONAL TRADE

(*As agreed upon by the International Committee for the Analysis of Artificial Manures and Feeding Stuffs at the International Congress of Applied Chemistry, Berlin,* 1903).

Preparation of the Samples for Analysis

As far as possible, a degree of fineness should be aimed at which will enable the whole of the material to pass through a 1 mm. sieve; this applies to all feeding stuffs without exception.

Methods of Analysis

1. **Moisture.**—Five g. of substance are dried at 100° for three hours. In the case of linseed cake, see under 3 (i).

2. **Albuminoids.**—(i) *Total Albuminoids.* Nitrogen is estimated by Kjeldahl's or Gunning-Atterberg's method, and the amount of nitrogen found is multiplied by 6·25. In the case of difficultly decomposable feeding stuffs, *e.g.*, cotton-seed meal, ground-nut meal, etc., it is advisable to add phosphoric anhydride to the acid if Kjeldahl's method is used.

(ii) *Pure Albumin* is estimated either by Stutzer's or by Kellner's method. The method used should be stated.

(iii) *Digestible Nitrogen Compounds.*—These are estimated by G. Kühn's improved modification of Stutzer's method.

Commercial pepsin may be substituted for gastric juice, provided the conditions laid down by Wedemeyer[1] are followed.

3. **Fat.**—(i) *General Method.* The feeding stuffs must first be dried for three hours at 95°, on no account above 100°. In the case of linseed cake and other oil cakes containing oils which oxidise easily, the drying must of course be conducted in a current of hydrogen or coal gas, or it must be limited to one hour at 100°. The fat must be extracted with ether free from alcohol and water. The extraction must be complete. The ether extract need not be soluble in ether after drying.

(ii) *Molasses Feeding Stuffs.* To estimate the fat, 25 g. of molasses feeding stuff are first dried for about three hours at about 80°, weighed when cold, and then ground; 5 g. of the powder are then placed on a filter or in a Gooch crucible attached to the pump, and extracted with 100 c.c. of cold water, which is allowed to drip slowly on to the substance. The residue is dried at 95° in the usual way and extracted with ether.

[1] *Landw. Versuchs-Stat.*, 1899, **51**, 385.

4. **Nitrogen-Free Extractive Matters.**—(i) The total of these products is generally taken by difference when all other constituents have been estimated.

(ii) In the estimation of sugars, the methods agreed upon by the International Sugar Commission are accepted.

5. **Woody Fibre.**—This is estimated by Weender's method of boiling 3 g. of substance (deprived of fat if necessary) with 200 c.c. of 1·25 per cent. sulphuric acid and 200 c.c. of 1·25 per cent. potassium hydroxide. Each boiling must be continued for half an hour from the moment when ebullition commences, and the water evaporated off must be replaced; each boiling with acid or alkali is followed by boiling with water. The residue is thoroughly washed with hot alcohol and then with ether, dried till of constant weight and weighed. The weight of the ash of the residue is subtracted.

6. **Ash.**—Five g. of substance is carefully incinerated at a gentle heat.

7. **Sand or Mineral Admixtures.**—The qualitative examination of all feeding stuffs for sand or mineral admixtures is necessary. These constituents must be quantitatively estimated whenever the preliminary test shows their presence in abnormal quantity. The sender of the sample must be informed of the result if the amount of these admixtures is more than 1 per cent.

As arising out of the methods described, the following observations may be offered:—

Oil. Attention has been already called to the recent substitution in the English official methods of petroleum spirit for ether, and to the reason for the alteration.

Fibre. On the other hand, the English regulations now adopt the "International" method (Weender's Method) for fibre. Most English analysts, for the last sixty years at any rate, had been in the habit of using smaller volumes of somewhat stronger solutions. The custom was to boil a suitable quantity (usually about 3 g.) of the material with 125 c.c. of 2 per cent. sulphuric acid solution, followed by boiling with a similar volume of 2 per cent. solution of potassium or sodium hydroxide. In America and on the Continent, however, the method (Weender's) agreed upon by the International Committee of 1903, prescribing successive boiling with 200 c.c. of 1·25 per cent. sulphuric acid and 200 c.c. of 1·25 per cent. potassium hydroxide, has been for some considerable time adopted, except for the substitution of sodium hydroxide for potassium hydroxide. It is to be noted that in the English regulations, the carrying out of the process is described in

more minute detail than in the briefly epitomised "International" directions, and correspondingly minute directions are given in the American Methods of Analysis.[1] In the English regulations, the analyst is directed to weigh the fibre on a previously dried and weighed filter paper, weighing (as is, of course, necessary under these circumstances) in a weighing bottle. It is more convenient and, as far as the experience of the writer goes, equally accurate to collect the fibre finally on the inner of two filter papers folded together and previously counterpoised against one another, the outer filter, after drying, being separated and used as a counterpoise to its companion in weighing the fibre. It has been objected that the fibre, if not protected by a weighing bottle, may regain moisture during the process of weighing. With a quickly acting balance and in the hands of a smart operator, however, the weighing can be sufficiently rapidly conducted to make any error of the kind indicated immaterial, in view of the range of variation between two determinations on the same sample made by the same operator, and having regard to the necessarily empirical nature of the estimation by a process involving the observance of so many details. For legal purposes, however, in this country the weighed filter and the weighing bottle must be adopted.

In the American method, the fibre is collected, filtered, and weighed in a Gooch crucible.

Distinction between Sand and "Natural Silica"

As a rule no distinction is made in the routine analysis of feeding stuffs between silica present as a natural constituent of vegetable tissues and adventitious silica in the form of sand, clay, etc.

Some natural materials, as, for instance, the husks of rice and the outer coatings of oats, contain appreciable quantities of silica. In the case of rice husks the quantity is large, amounting sometimes to 20 per cent. of the rice "shude" or husk.

In the ordinary commercial analysis of rice bran, no differentiation is usually made between this and adventitious silica, the percentage of total silica having indeed been adopted in commercial transactions as a rough indication of the extent of inclusion in rice bran of the shudes or husks which should be eliminated, but which by some rice millers are improperly ground up and mixed in various proportions in what is sold as rice bran. As a check on this, a deduction is made from the price payable per ton on a sliding scale increasing with the percentage of total siliceous matter present in officially drawn samples. Sometimes, however, there are reasons for distinguishing between adventitious sand and such silica as may

[1] *Off. Methods of Anal. Amer. Assoc. Agric. Chem.*, 1925, p. 118.

be derived from vegetable tissues. This differentiation may be approximately made as follows:—

The total siliceous matter is determined in the ash by moistening with hydrochloric acid, evaporating to dryness, taking up with dilute hydrochloric acid (one of strong acid and three of water), boiling for fifteen minutes, filtering, washing and weighing the total insoluble matter after ignition. The total silica, etc., thus obtained is boiled with 100 c.c. of a 10 per cent. solution of anhydrous sodium carbonate for ten minutes, filtered, washed once with cold 10 per cent. sodium carbonate solution, then with boiling water till free from alkali, then with dilute hydrochloric acid, and again with water, dried, ignited and weighed. The matter insoluble in sodium carbonate thus weighed will contain a little less than the whole of the adventitious "sand," seeing that sodium carbonate is not altogether without action on sand or other siliceous matters of mineral origin and that this action is partly dependent upon the fineness of the sand, etc. On the other hand, the carbonate solution used as indicated fails to dissolve some small proportion of the natural silica derived from husks. The average plus and minus errors from these two sources may be taken as being approximately compensated for in the following formula, which is based upon the empirical experience that about 8 to 9 per cent. of the silica derived from the vegetable tissue is left undissolved by the sodium carbonate, whereas there is left undissolved from 96 to 97 per cent. of extraneous or adventitious silica:—

If S be the original sand or extraneous siliceous matter, A the original weight of total siliceous matter and B the matter left undissolved by the soda,

$$S = \frac{B - 0.085\,A}{0.88}.$$

When it is necessary to make the distinction, however, it is well for the analyst while returning the exact figure for total sand and other siliceous matters to state that this total includes "approximately" such and such a quantity of sand or adventitious silica as distinguished from the natural silica of the husks, without affecting any close accuracy in decimal places.

Differentiation between "Total Albuminoids," as Conventionally Stated, and "True Albuminoids"

The following method has been described by Stutzer:—One hundred c.c. of water is poured on to 1 to 2 g. of the sample in a beaker, the liquid heated to boiling, or when the material contains starch, heated in a boiling water-bath for ten minutes, then treated with 0·3 to 0·4 g. of cupric hydroxide suspended in water, filtered when cold,

and the residue on the filter thoroughly washed with water. The nitrogen is determined in the insoluble residue and taken as true albuminoid nitrogen. When the feeding stuffs are rich in alkali phosphates (*e.g.*, oil-cake, meal, bran), 1 c.c. of alum solution (1 : 10) is added to the hot liquid before adding the cupric hydroxide. The potassium is thus combined as sulphate, and so rendered incapable of dissolving albumen and preventing its precipitation.

Barnstein,[1] modifying a process by Kellner, suggested an improvement on Stutzer's method as follows:—The substance is boiled or digested with hot water and 25 c.c. of copper sulphate solution, containing 60 g. of crystallised copper sulphate per litre, is added. Then 25 c.c. of diluted sodium hydroxide solution (12·5 g. per litre) is slowly added with stirring, the precipitate allowed to settle and then treated as in Stutzer's method.

The concentrations of the copper sulphate and sodium hydroxide solutions are chosen so that the whole of the copper is not precipitated by the alkali, while the precipitate produced contains as much effective cupric hydroxide as is used in Stutzer's method. One advantage claimed for this method is that the precipitate generally settles more rapidly and completely than is the case in Stutzer's method. The results obtained by the two methods agree in the case of most feeding stuffs.

In America[2] the method adopted is as follows:—Copper sulphate is dissolved in water in the proportion of 20 g. of copper sulphate to 1 litre of water with the addition of a small quantity of glycerol. A 20 per cent. solution of sodium hydroxide is then added until the liquid is slightly alkaline, the copper hydroxide is filtered off, rubbed in a mortar with water containing 0·5 per cent. of glycerol and washed by decantation or filtration until the washings are no longer alkaline. The precipitate is again rubbed in a mortar with water containing 10 per cent. of glycerol, thus preparing a uniform gelatinous mass that can be measured with a pipette. The quantity of copper hydroxide in 5 c.c. of the mixture is approximately determined by diluting, filtering, washing, igniting and weighing as copper oxide. The determination of albuminoids is carried out as follows:—

Place 0·7 g. of the sample in a beaker, add 100 c.c. of water and heat to boiling; or in the case of substances rich in starch, heat on a steam-bath for ten minutes; add such a quantity of the cupric hydroxide reagent as contains about 0·5 g. of the hydroxide; stir thoroughly, filter when cold, wash with cold water, and without removing the precipitate from the filter, determine the nitrogen therein by the Kjeldahl process. If the material (such as seeds or oil cake) is rich in

[1] *Landw. Versuchs-Stat.*, 1904, **54**, 327.
[2] *Off. Methods of Anal. Amer. Assoc. Agric. Chem.*, 1925, p. 116.

alkali phosphates 1 to 2 c.c. of a 10 per cent. solution of ammonium-free soda alum is added, prior to the cupric hydroxide reagent, to decompose the alkali, on the ground that if this is not done copper phosphate and free alkali may be formed and the protein-copper precipitate partially dissolved in the alkaline liquid.

Digestible Albuminoids.—Attempts have been made to arrive at the degree of digestibility of albuminoids by laboratory methods. Stutzer introduced a method for artificial digestion with gastric juice, which method was subsequently improved by Küln and Kellner. In this method the digestion liquid is prepared as follows:—

The mucous membranes of ten pigs' stomachs are cut with scissors into fine strips, 49 litres of water and 1 litre of 12·5 per cent. hydrochloric acid poured over them and left to digest, with frequent shaking, for two to three days in a cool place. The liquid is then poured off through a small flannel bag and finally filtered through a double folded filter. As a preservative, 0·5 per cent. of chloroform is added to the digestion liquid, which is stored in closed vessels in a dark place.

Digestion is conducted by pouring 500 c.c. of the digestion liquid on to 2 g. of the substance under examination and warming to 37° to 38° on a water-bath or in an incubator. After about twelve hours, 10 c.c. of 12·5 per cent. hydrochloric acid is added and the same addition repeated after twenty-four and thirty-six hours, so that at the end of this time the liquid contains approximately 1 per cent. of hydrochloric acid. After the lapse of a further twelve hours the digestion liquid is filtered from the undissolved substance, the latter washed with water, alcohol and ether, and together with the filter paper, decomposed with 30 c.c. of sulphuric acid by Kjeldahl's method; the percentage of undigested nitrogen is thus estimated. A blank experiment should be made. As an alternative, half the hydrochloric acid to be used may be added at the beginning of digestion and the other half after the lapse of twenty-four hours. The liquid must be frequently stirred during digestion, and the vessel covered to prevent evaporation.

K. Wedemeyer[1] has devised a method in which commercial pepsin is substituted for gastric juice. The pepsin must conform to the test prescribed by the German Pharmacopœia III., viz., "An egg is placed for ten minutes in boiling water and then allowed to cool; when cold, the white is rubbed through a sieve suitable for the preparation of a coarse powder. Ten g. of the white of egg thus broken up is mixed with 100 c.c. of warm water at 50° and ten drops of 25 per cent. hydrochloric acid; 0·1 g. of pepsin is then added. The mixture is kept for an hour at 45° with frequent shaking; at the end of this time the white of egg must have completely disappeared, with the exception of some

[1] *Landw. Versuchs-Stat.*, 1899, **52**, 375.

slight whitish yellow membranes." If the pepsin does not dissolve to a perfectly clear solution in 0·5 per cent. hydrochloric acid, the solution must be filtered.

Wedemeyer gives the following directions for the digestion:—2 g. of the feeding stuff is placed in a beaker and treated with 490 c.c. of a clear solution, containing 1 g. of pepsin and 10 c.c. of 25 per cent. hydrochloric acid. The beaker is covered with a glass plate and digested at 37° to 40° for forty-eight hours, with frequent stirring. Ten c.c. of 25 per cent. hydrochloric acid is added after the lapse of twenty-four hours, thus bringing up the amount of acid to 1 per cent. When digestion is complete, the undissolved substance is collected on a filter and washed with warm water until the filtrate no longer contains chloride; it is then washed with alcohol, and finally very thoroughly with ether. The nitrogen in the undissolved substance and filter is then estimated. A blank experiment should be made.

Pentosans.—By pentosans are meant, in feeding stuffs, those carbohydrates which give furfural on distillation with hydrochloric acid. Methods of estimation have been described by B. Tollens.[1] Of these only the simplest, the phloroglucinol method, will be described[2]; it is carried out as follows:—

Two to 5 g. of the substance under examination is placed in a flask of about 300 c.c. capacity, and distilled with 100 c.c. of hydrochloric acid (sp. gr. 1·06) over a bath of Rose's metal (one part each of lead, tin, and bismuth). Thirty c.c. of liquid is distilled off and then replaced in the distillation flask by 30 c.c. of the same acid; 30 c.c. is again distilled off, and this operation is continued until the distillate amounts to nearly 400 c.c. Pure phloroglucinol, dissolved in a little hydrochloric acid (sp. gr. 1·06) is added to it, to the extent of double the amount of furfural expected, the solution diluted with the same acid to 400 c.c., stirred round, left to stand till the next day, filtered through a Gooch crucible fitted with asbestos, the precipitate washed with 150 c.c. of water at 15° to 20°, dried for four hours in a water-jacketed drying oven and weighed.

Tollens calculates the amount of furfural from the weight of the precipitate if the amount is small, by dividing by 1·82. If the amount is large, he divides by 1·93. This is somewhat vague. E. Kröber has subjected the method to critical examination, and has worked out a table which enables the amount of pentosans corresponding to the weight of phloroglucide found to be read off directly.[3] His formulæ are as follows:—

[1] *Landw. Versuchs-Stat.*, 1893, **42**, 381, 398; *Z. Ver. Rübenzuckerind*, 1894, **44**, 460.

[2] For another method, see Whitaker and Powell, *J. Soc. Chem. Ind.*, 1924, **41**, 35 T.

[3] *J. für Landwirtschaft*, 1900, p. 357; see also *Off. Methods of Anal. Amer. Assoc. Agric. Chem.*, 1925, p. 121.

(1) For a weight of phloroglucide (designated by "a" in the following formulæ) under 0·03 g.:—

Furfural $= (a + 0.0052) \times 0.5170$.
Pentoses $= (a + 0.0052) \times 1.0170$.
Pentosans $= (a + 0.0052) \times 0.8949$.

In the above and also in the following formulæ, the factor 0·0052 represents the weight of the phloroglucide that remains dissolved in the 400 c.c. of acid solution.

(2) For a weight of phloroglucide "a" between 0·03 and 0·3 g., use the following formulæ:—

Furfural $= (a + 0.0052) \times 0.5185$.
Pentoses $= (a + 0.0052) \times 1.0075$.
Pentosans $= (a + 0.0052) \times 0.8866$.

(3) For a weight of phloroglucide "a" over 0·3 g.:—

Furfural $= (a + 0.0052) \times 0.5180$.
Pentoses $= (a + 0.0052) \times 1.0026$.
Pentosans $= (a + 0.0052) \times 0.8824$.

Starch.—The determination of starch is most conveniently effected by Ewer's Method.[1] Five g. of the feeding stuff is washed with cold water on a filter to remove sugar and other water-soluble carbohydrates. The insoluble matter is washed into a flask with 50 c.c. dilute hydrochloric acid containing 1·125 per cent. by weight of hydrogen chloride and digested in a boiling water-bath for 15 minutes with repeated shaking during the first three minutes. The liquid is then made up to 90 c.c., cooled to 20° and precipitated with 10 c.c. of a 4 per cent. solution of phosphotungstic acid, made up with water to 100 c.c., well shaken, allowed to settle, filtered and the rotation of the filtrate determined polarimetrically at 20° in a 200 mm. tube in a half shadow quartz compensating polarimeter (Vol. I., pp. 203 *et seq.*).

The soluble starch product obtained by this method, calculated for the weight of original dry starch, has a rotation of αD 181°·5. Consequently on the assumption that the reading is taken as prescribed in a 200 mm. tube on the clear filtrate obtained as above from 5 g. of original material each angular degree is indicative of 5·51 per cent. of starch.

If the polarimeter has been constructed for sugar work and graduated in Ventzke divisions, 1 Ventzke division, being approximately equal to 0°·347 angular degrees, may be taken as indicating 1·912 per cent. of starch. On French instruments constructed on the Soleil Duboscq type, bearing a sugar scale for a normal weight of 16·35 g. of sugar (instead of 26 g. as with the Ventzke instrument), each sugar-

[1] *Z. öffentl. Chem.*, 1908, **14**, 8, 150; *Z. ges. Brauw.*, 1908, **31**, 250.

scale division, under the conditions above laid down, may be taken as indicating 1·2 per cent. of starch.

An alternative process is the Diastase Method. A portion of the feeding stuff is washed with cold water and the starch converted into its hydrolysis compounds by digestion either with Tacca diastase or with a measured volume of a malt extract. After digestion under appropriate conditions, the insoluble matter is separated by filtration and washing, and in a measured volume of the filtrate, the "extractive" carbohydrates brought by boiling with diluted acid into the form of dextrose, which is then determined in the usual way. If malt extract has been used, the dextrose derived from the volume of malt extract used in the estimation must, of course, be separately determined and deducted from the total. For full details see the section "Starch," Vol. VI. of this work.

II. GREEN FODDER, HAY AND STRAW

The main difficulty here is in obtaining a fair sample of the bulk. The sample should be collected from many different parts of the bulk and passed through a chaff-cutter, the resulting chaff being thoroughly well mixed and "quartered down" for a sample.

The "rough" moisture is determined in a large average portion of the sample. The dry fodder is reduced by any convenient grinding apparatus into a state sufficiently fine for analysis. During the process of grinding it will have regained some of its lost moisture, and this must be determined and allowed for in calculating the analytical results to the dry state and to the original condition of the fodder. The analysis is conducted as for concentrated feeding stuffs, pp. 562-67.

III. FODDER ROOTS (MANGOLDS, BEETS, TURNIPS, ETC.)

Thin radial vertical sections should be cut from many roots. The slices are rapidly weighed and then suspended in a row on a string until they have become "air-dried." They are then weighed and the lost moisture thus determined.

The air-dried slices which still contain a good deal of moisture are rapidly ground to a condition suitable for analysis. The moisture is determined in the ground sample. From the data obtained, the approximate percentages of water and dried matter in the original roots are arithmetically calculated. The analysis of the powder is made as for feeding stuffs.

In determining, when this may be considered necessary, the small quantity of oil present, it is necessary first to wash out the sugar as directed in the analysis of concentrated "sugar feeds."

In roots, as for example in sugar beet, the determination of sugar is carried out separately on pulp obtained from the undried root. This pulp may be prepared by rapidly passing a number of vertical radial sections of the root through a mincing machine or by the use of a rasp, but where, as in a beet-sugar factory, or elsewhere, many roots have to be tested for accurate comparison, a special mill is used which rapidly cuts from each root presented to it a radial section directly in the form of pulp.

Sugar is usually determined polarimetrically, or some modification of Fehling's method, either gravimetric or volumetric, may be used. (See under Sugar, Vol. VI.).

IV. MOLASSES FEEDING STUFFS, OR SUGAR FEEDS

These consist of fibrous materials saturated with molasses, the fibrous matter being used simply as a vehicle for the convenient handling of the molasses and its consumption as fodder. Dried finely shredded peat moss, the finely shredded pith of the sugar cane, spent hops and a variety of other materials are in use as a vehicle for the molasses.

The sugar in these sugar feeds may be determined as already indicated in the English Official Methods (p. 556).

Mineral Adjuncts to Feeding Stuffs

Various mineral additions are sometimes made to mixed meals for certain purposes, as for pigs or for young cattle. These include or consist mainly of calcium phosphate, sometimes in the form of bone ash, but more frequently in the more readily digestible form of "precipitated" phosphate, *i.e.* di-calcium hydrogen phosphate precipitated by means of lime from the acid solution obtained as a by-product in the manufacture of glue or gelatine. In such materials the analyst is not only called upon to determine the phosphoric acid and lime as in a fertiliser, but usually also to examine for contamination with arsenic derived from the acid used in its preparation.

Arsenical Contamination. Arsenic may be approximately assessed by the Gutzeit method, as laid down in the British Pharmacopœia:—

Two g. of the phosphate is dissolved in 10 c.c. of cold stannated arsenic-free hydrochloric acid (*i.e.* pure strong hydrochloric acid in which has been dissolved 0·2 g. pure tin per 100 c.c. of acid). This is diluted with 50 c.c. of water and placed in a 4-oz. bottle closed with an indiarubber perforated stopper in which is fixed a narrow vertical tube in which has been inserted a strip of filter paper previously saturated with lead acetate and dried. Over the mouth of the tube is fixed, by means of an indiarubber band, a piece of

porous filter paper previously dipped into mercuric chloride solution and dried. Ten g. of pure granulated zinc is dropped into the bottle containing the solution, which is immediately closed by the india-rubber stopper, and the yellow stain, if any, produced on the coloured mercurised paper by any evolved arseniuretted hydrogen during half an hour is compared against that similarly obtained with a dilute standard solution of arsenious acid. If the stain is too deep for convenient comparison, a smaller quantity of the phosphate is taken or a small aliquot part of a measured solution of a suitable quantity of the phosphate. More detailed precautions will be found in the British Pharmacopœia. For accurate purposes the indication thus obtained should be confirmed by the Marsh-Berzelius process or its electrolytic modification. (Vol. I., p. 433 *et seq.*)

Iodine. Potassium iodide in small quantities is sometimes a constituent of mineral or saline mixtures for use in feeding stuffs. Iodine may be determined in an aqueous solution of the mixture by liberating the iodine in a free state by addition of a small quantity of sulphuric acid previously saturated with nitrogen peroxide. The iodine thus liberated may be extracted by shaking up in a separator with successive quantities of carbon disulphide. The iodine may be estimated by the colour of its carbon disulphide solution (sufficiently diluted) against a known quantity of iodine in similar solution.

Detection of Mustard in Feeding Stuffs

Wild mustard seed is frequently present as an impurity in rape seed and the admixture may be sufficiently large to make cake or meal even fatally poisonous by reason of the irritation caused by the volatile oil of mustard developed after ingestion of the cake. This impurity may be detected by mixing 10 g. of the finely ground cake or meal with cold water to a thin paste in a bottle, corking it and allowing it to stand in a warm place (say on the top of a water oven) for a couple of hours. The contents of the bottle having been allowed to cool somewhat, the cork or stopper is removed, when the smell and taste of the paste will indicate whether it is or is not fit for feeding purposes owing to the development of the pungent volatile oil of mustard. Förster has suggested the following method of determining the quantity of mustard oil generated in seed contained in cake or meal contaminated with mustard.

Twenty-five g. of the cake meal is stirred up with 150 c.c. of water in a flask; if necessary, white mustard must be added. The flask is closed by a ground stopper, into which two glass tubes are fused; one conducts steam into the mixture, the other leads the vapours to a condenser, with which an air-tight joint is made. After standing for half an hour, steam is passed into the flask and the distillate collected

in a receiver fitted with an air-tight connection to the condenser; in the receiver is placed 50 c.c. of alcoholic ammonia, with which the mustard oil combines to form allyl-thiourea, which is difficultly volatile.

When about 200 c.c. of liquid has distilled over, the condenser water is turned off, and alcohol vapour passed through the condenser tube until it is thoroughly washed. The contents of the receiver are well mixed, left to stand for twelve hours, transferred to a large beaker and heated to boiling; 0.8 g. of freshly precipitated mercuric oxide is then added and the liquid kept boiling for a few minutes longer, bumping being prevented by continual stirring. The mercuric oxide is prepared by adding an excess of potassium hydroxide to 25 c.c. of 4 per cent. mercuric chloride solution and heating to boiling; the precipitate and liquid are used together.

Twenty-five c.c. of 4 per cent. potassium cyanide solution is added before the liquid has completely cooled, to dissolve the excess of mercuric oxide and the dimercuric-ammonium hydroxide formed, and the liquid stirred round for a few minutes. The precipitated mercuric sulphide is collected on a weighed filter, washed with hot water, dried at 100° to 110° and weighed. The weight of mercuric sulphide, multiplied by 0.4266, gives the amount of volatile mustard oil (allyl thiocyanate, C_3H_5CNS).

A later method is that of Schlicht,[1] being a development of his own earlier modification of a method of V. Dircks,[2] which consisted in the oxidation of the distilled mustard oil to sulphate by alkaline permanganate. Schlicht proceeds as follows:—25 g. (or less if much mustard oil is present) of the feeding stuff is digested with water for four hours at the ordinary temperature in a flask connected with a condenser and a receiver which contains 50 c.c. of a saturated solution of potassium permanganate with the addition of potassium hydroxide equivalent to one-fourth of the weight of the permanganate in solution. The mixture in the flask is boiled for fifteen minutes, cooled, a solution of myrosin added and allowed to act for sixteen hours, after which the solution is steam distilled.

Alternatively, 25 g. of the meal may be digested for sixteen hours at the ordinary temperature with 300 c.c. of water containing 0·5 g. of tartaric acid and then steam distilled. The permanganate solution which has received the distillate (by which its volume will have been increased by 150 to 200 c.c.) is then shaken and the excess of permanganate reduced by the addition of pure alcohol. The whole liquid is made up to a known volume, filtered and the sulphate produced by the oxidation of the mustard oil determined after acidification by hydrochloric acid in the usual way as barium sulphate. The addition

[1] *Z. öffent. Chem.*, 1903, **9**, 37. [2] *Landw. Versuchs-Stat.*, **28**, 179.

of a little iodine is suggested after acidification in case any sulphite should be present. The barium sulphate is calculated to its sulphur equivalent of essential oil of mustard.

Hydrocyanic Acid.—Certain beans, mostly of tropical or sub-tropical origin, sometimes offered for feeding purposes, contain cyanogenetic glucosides which under the action of their accompanying enzymes, evolve hydrocyanic acid in the intestinal canal, and consequently exert a poisonous action. Linseed also gives rise to the same acid, but the activity of the enzyme of linseed is to a considerable extent checked by the heat applied to ground linseed before it is converted into cake by the expression of the oil.

The literature relating to the whole question of the occurrence of cyanogenetic glucosides in food stuffs and the extent to which they may become objectionably decomposed under various conditions is extensive; the Journal of the South-Eastern Agricultural College at Wye contains a comprehensive discussion of the subject in the report of S. J. M. Auld in No. 20 of that Journal (April 1912).

For the detection of hydrocyanic acid, Guignard[1] recommends the alkaline picrate test, viz.: the red colour reaction produced on a test-paper prepared by dipping filter paper first into a 1 per cent. aqueous solution of picric acid and then, after drying, in a 10 per cent. solution of sodium carbonate. To carry out the test a few grams of the powdered beans or other meal are moistened with water in a stoppered bottle in which a strip of the test paper is suspended, the closed bottle being then kept for a few hours at a temperature which should not exceed blood heat.

Chaston Chapman[2] has shown that this reaction, though delicate, is not specific for hydrocyanic acid, but is merely a reduction reaction which may be effected by other volatile compounds produced by fermentation. Although the reaction is not, therefore, conclusive in a positive direction, on the other hand the absence of coloration may be regarded as conclusive of the absence of any emanation of hydrocyanic acid.

An alternative or confirmatory colour test may be performed by substituting for the picrate paper a strip of paper which has been freshly dipped first into a 0·2 per cent. tincture of guaiacum resin and then in a 0·1 per cent. solution of copper sulphate. A blue colour is developed in presence of hydrocyanic acid vapour. The test is very delicate.

The total quantity of potential hydrocyanic acid in the feeding stuffs under examination (as apart from the extent to which it may be spontaneously liberated by the action of any accompanying enzyme) is determined by the preliminary extraction of the

[1] *Comptes rend.*, 1906, **142**, 545. [2] *Analyst*, 1910, **35**, 469.

glucosides with alcohol, as described by Henry and Auld,[1] as follows:—

Twenty-five g. of the ground material is placed in a Soxhlet apparatus and extracted for twenty-four hours with boiling alcohol. The alcohol is evaporated from the extract with addition of a little water. Sufficient 10 per cent. sulphuric acid is then added to bring the concentration of the acid to approximately 6 per cent. in a total volume of 50 c.c. Henry and Auld recommended a weaker concentration of acid but subsequent experience indicated that the liberation of the hydrocyanic acid was expedited by increasing the concentration to 6 per cent. The hydrocyanic acid is then distilled off. The distillation flask should be furnished with a tap funnel whereby the volume of liquid may be kept fairly constant during distillation, the end of the condenser dipping into a dilute solution of sodium hydroxide. Henry and Auld recommend titration of the alkaline distillate with dilute silver nitrate solution according to the well-known method of Liebig (see "Analysis of Cyanides," Vol. I., p. 624). A convenient strength of silver solution is $N/50$, 1 c.c. of which is equivalent to 1·08 mg. of HCN.

An alternative method is to evaporate the distillate (made strongly alkaline in this case) with 0·5 g. of ferrous sulphate, thus converting the cyanogen into sodium ferrocyanide, the filtered alkaline solution of which may be acidified and the quantity of ferrocyanide assessed by the colour produced on addition of a ferric salt in a suitable dilution using a standard solution of dilute potassium ferrocyanide for comparison.

Another alternative method is to evaporate the distillate (made strongly alkaline with sodium hydroxide) to dryness with the previous addition of a little yellow ammonium sulphide, take up with water, acidify with hydrochloric acid, filter if necessary, and estimate the thiocyanate colorimetrically with ferric chloride.

The hydrocyanic acid capable of being liberated by the spontaneous action of the naturally accompanying enzyme in the feeding stuff is ascertained as follows: 250 c.c. of water is placed in a round-bottomed flask of about 1·5 litres capacity, a few drops of toluene added and the temperature raised to about 38°. A weighed quantity of the finely ground cake or meal (25 to 50 g.) is then introduced into the flask and mixed by shaking. The flask is stoppered with a rubber bung and placed in a thermostat for twelve hours at a temperature of about 38°. After this period of digestion, the contents of the flask are steam distilled into a saturated solution of sodium bicarbonate.

Reducing products of fermentation which may be distilled over are in this case apt to interfere with the "end point" if titration with silver

[1] "Occurrence of Cyanogenetic Glucosides in Feeding Stuffs," *J. Soc. Chem. Ind.*, 1908, **27**, 428.

nitrate is adopted, although no such difficulty occurs when the glucoside has been preliminarily extracted as in the determination of total potential hydrocyanic acid. Henry and Auld therefore prefer in the estimation of the spontaneously generated (or as it is sometimes called "free") hydrocyanic acid, to titrate with $N/50$ iodine solution until the faintest perceptible colour is produced. Each c.c. of solution required equals 1·35 mg. HCN.

Alternatively, the distillate may be collected in fairly strong sodium hydroxide solution (instead of sodium bicarbonate) and evaporated with the addition of ferrous sulphate (or of ammonium sulphide) and the estimation made colorimetrically as already described.

Detection of Castor-Oil Seed.

Oil-cakes or meals made in tropical or subtropical countries are liable to contamination with castor-oil seed (*Ricinus communis*) occasionally to an extent sufficient to render the feeding stuff poisonous. The lighter contaminations are usually due to the harvesting of wild or accidentally grown castor-oil seeds with the crop, but contamination sometimes occurs through carelessness in mills in which castor-oil seed as well as linseed or ground nuts or other oil seeds may be habitually crushed. Merchants purchasing such cakes or meals usually insert in their contracts stringent clauses against the presence of castor-oil seed even in minute quantities. The analyst of feeding stuffs is therefore constantly called upon to ascertain the presence or absence of castor-oil seed. For this purpose the following procedure should be followed:—500 g. of the crushed cake (or meal) is a suitable quantity to take for examination. For convenience, this should be divided into two portions of 250 g. each and each portion treated separately, thus arriving at duplicate results. Each of these portions is placed in a vessel capable of holding from 2 to 2½ litres, a large earthenware jug of "pitcher" form being a convenient vessel for the purpose. 100 c.c. of concentrated hydrochloric acid is poured into the jug and diluted with boiling water, the contents being well stirred. After about 15 to 30 minutes the mixture is allowed to settle for a short time, the top liquor poured off and the jug filled up with boiling water, which, after settling, is poured off; this washing by decantation is repeated two or three times. About 30 g. of sodium hydroxide dissolved in water is then put into the vessel, diluted with boiling water and the process of washing proceeded with as before. The residue in the jug then consists mainly of fibrous matter. About 30 g. of bleaching powder is then made up to a cream with 500 c.c. of cold water, and after frequent stirring allowed to settle, when the supernatant liquid is poured on to the residue of the cake or meal in the jug, which is then left for an hour or two, or, if more convenient, over-night.

The seed coats of most of the oil seeds in commerce are bleached by this process, or sufficiently bleached to form a sharp contrast with any fragments of the testa of castor-oil seed, which are so far unaffected by the treatment as to lose only their delicate, thin, mottled outer membrane, remaining as dark brown angular brittle fragments which appear black in water and are easily recognisable by microscopical examination. In order to separate these particles, the contents of the jug, portion by portion, are poured into a large white photographic dish with a spout at the corner, the bleached particles being washed away by treatment with successive quantities of water. The particles of castor-oil seed "husk" (as it is colloquially miscalled, not being really a "husk" but the testa of the seed), being heavy, remain at the bottom of the dish. In this way the whole of the material in the jug is treated, all approximately black particles being picked out with a fine forceps for microscopical examination. The whole of the castor-oil seed fragments thus obtained from the 250 g. of cake or meal are dried and weighed. The dry weight of the fragments after the foregoing treatment multiplied by 5 gives a near approximation to the weight of original castor-oil seed which they represent. It is customary to return the results by saying that such and such a quantity, say 500 g. of the cake or meal, taken as a fair average portion of the sample, "contained such and such a percentage of castor-oil seed 'husk' equivalent to such and such a percentage of original castor-oil seed."

Biological "precipitin" tests have been proposed for the recognition of the active principle of castor-oil seed by the action of a saline extract of the meal on defibrinated blood. This test is extremely delicate when castor-oil seed alone is tested, but unfortunately when only a small quantity of castor-oil seed is mixed with an overwhelming proportion of other seeds or feeding stuffs, the precipitin reaction of the active principle of the castor-oil seed is so interfered with or obscured as to render this test in most cases useless for practical purposes. The analyst must therefore rely upon the concrete evidence furnished by the presence of the characteristic "husk" or testa of the seed as already indicated.

A word of warning may be given to the analyst not to mistake for the testa of the castor-oil seed fragments of grape-seed derived from grape-seed cake which sometimes, though rarely, finds its way into compound cakes or meals. Some of these fragments bear a superficial resemblance to those of the stripped testa of *Ricinus*, and even under the microscope some skill is required in their differentiation. The grape-seed particles, after treatment as already described, remain unaffected by bleaching powder solution, being in this respect like those of *Ricinus*. But, unlike the latter, grape-seed particles are much lightened in colour by soaking in a 10 per cent. solution of sodium hydrosulphite, and

in doubtful cases the fragments should be thus examined side by side with known fragments of *Ricinus*. In this connection it may be noted that if grape-seed cake has been deliberately used as a constituent of the meal under examination, it would be present in substantial quantities as compared with such relatively small quantities of castor-oil seed as would be present as a mere contamination, so that the mere abundance of the fragments found should serve as a warning against too hasty a conclusion.

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SOILS

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THE classification of soils has been of late years subjected to an entire revision in the light of the work of Sibirtzev, Glinka and the Russian school of soil chemists. In that extensive dominion students of the soil have had the opportunity, not only of seeing a great diversity of soil types, but also of deducing the origin of these types under the influence of climate, and the main conclusions they have reached have been confirmed and extended by observations in other countries, notably in the United States. Broadly speaking, it is now seen that the soil type is an expression of the climate, particularly of the rainfall and temperature; a particular group of climatic conditions ultimately gives rise to a uniform type of soil whatever the prime rock materials out of which it is formed, whether in the old world or the new. Within the limits of the type there may be many variations, often of dominant importance to the cultivator. For example, the West European temperate countries, like the British Isles, mainly possess what are termed "brown earths" and "ash" soils, originating under moderate temperatures and a rainfall sufficient to leach out most of the soluble products of rock weathering, but these soils may embrace sands, clays and silt soils, depending upon the parent rock from which they originated and requiring very different treatment both in cultivation and manuring.

The fundamental minerals from which the soil materials are derived consist mainly of various complex silicates of the sesquioxides (aluminium and iron) with the alkalis (sodium and potassium) and the alkaline earths (calcium and magnesium). Among the chief may be enumerated the felspars, the micas, hornblende, augite and olivine. These, with quartz, constitute in the first instance the igneous rocks like basalt and are reassembled in the metamorphic rocks like gneiss. In the more or less weathered condition they are also found in sedimentary rocks, where also occur considerable deposits of carbonate of lime, like chalk and limestone. Under the action of water, especially when it contains carbon dioxide derived from the air and the surface

soil, these silicates all decompose, the alkalis and the alkaline earths first going into solution, then some of the silica, and lastly the oxides of aluminium and iron. The nature of the resulting soil will depend upon the extent to which the original decomposition, itself largely determined by temperature, is followed by a leaching out of the soluble products. Under tropical conditions with high rainfall the alkalis and alkaline earths are very completely removed as carbonates and bicarbonates, which further bring about the solution of the silica, so that the resulting soil consists almost wholly of the sesquioxides. The high temperature also favours the rapid oxidation of all residues of vegetation, so that the soils are poor in organic matter. They are known as *laterites* and are generally bright red in colour.

With a lower rainfall the soluble salts are not washed out but accumulate in the lower layers of the soil, and may return to the surface as the soil water evaporates. Thus arise the alkali soils in which the soluble materials may either be neutral salts (*Solonschak*) or alkaline carbonates (*Solonetz*). Since part of the humus produced by the decay of vegetation is soluble in alkaline solutions this may also be carried down into a lower layer of the soil, giving rise to black alkali soils.

Under semi-arid steppe conditions when the rainfall in the early part of the year permits of considerable growth of vegetation which is protected from decay by the later drought, organic matter tends to accumulate. Hence arise the black earths or *tschernozems* of the prairies and the Russian steppes, often of considerable depth and great richness in organic matter, nitrogen and lime. Under more arid conditions the accumulation of organic matter is less and the chestnut-coloured earths result, which with increasing dryness become lighter in colour and pass by degrees into the alkali soils. Under moist temperate conditions the alkalis and alkaline earths are removed, the destruction of the organic matter is less, but by its action some of the sesquioxides go into solution. These may either be redeposited throughout the weathered material ("brown earths") or may be deposited in a layer or pan immediately below the bleached surface soil. These *Podsols*, to use the Russian nomenclature, include most of the soils of Great Britain. Finally, when the rainfall is so great as to saturate the soil, and produce anaerobic conditions, the organic matter of vegetation does not decompose and "peats" acccumulate. These may be either sour peats as on the high moorland or neutral peats in the marshes where the water is charged with carbonate of lime. Under these anaerobic conditions also ferric compounds are reduced to ferrous and sulphates to sulphides; the water also contains iron in the form of ferrous bicarbonate.

The scientist who is called upon to give advice with regard to soils may have either of two problems put to him. He may be asked for what crop or crops a given soil is suited or the more specific question of whether it will carry a particular crop. On the other hand, he may be asked what is wrong with a given soil, what makes it show general infertility or some special undesirable characteristic. The former problem usually obtains in the new countries, the latter among older established farming like our own. The soil chemist is rarely in a position to answer either question from the examination of a sample of soil in a laboratory, if only because the soil is but one factor in the very complex adaptation of a plant to its environment, in which situation and climate play equally important parts. Even the limited question of whether the soil is deficient in some particular element of fertility, *e.g.*, phosphoric acid, is only in extreme cases answerable by the analysis of an isolated sample. The ascertainable fact that a soil contains 1 per 1000 of phosphoric acid gives by itself no information as to whether the crop is in need of a phosphate fertiliser. In Great Britain it will be necessary to know whether 1 per 1000 is above or below the phosphate usually found in soils of the same sub-type, and also whether soils of that sub-type do or do not as a rule respond to phosphate fertilisers, a fact that is only ascertainable by experience or actual experiment.

In studying the first type of question, the most valuable guidance will be obtained from an examination of the soil *in situ*. The normal vegetation it carries affords important indications both as to fertility and the drift of land water within the soil, the necessity of drainage, etc. Next a hole must be dug well into the subsoil and the "soil profile" carefully exposed and recorded. On the interpretation of soil profiles, Comber, *The Scientific Study of the Soil* (1927), or Ramann, *Bodenkunde* (1911), may be consulted. The soil sample may then be taken, to be subjected in the laboratory to all or some of the following determinations. The mechanical analysis determines the size and distribution of the ultimate particles which make up the soil. This analysis gives precision to the usual classifications of soils as heavy or light, into clays, loams and sands, but it reveals also certain peculiarities in the working of the soil such as those caused by the predominance of the "silt" fraction, which causes a soil to slip readily during rain and set afterwards to a hard crust. Many attempts have been made to obtain by a single determination some measure of the relations of the soil to water, *e.g.*, its absorptive power or retentiveness. It cannot, however, be said that any of these methods for the measurement of "moisture holding capacity," "hygroscopic coefficient," "moisture equivalent," "wilting coefficient," etc., yield a figure either of absolute or of practical value. The chemical analysis which follows determines the amount of

organic matter, nitrogen, phosphoric acid, potash and calcium carbonate present in the soil. It is often desirable also to determine the more active forms of these constituents on which depend the immediate fertility of the soil or its "condition." To this end determinations may be made of the nitrates present, and of the phosphoric acid and potash soluble in weak acids. A determination of the acidity or rather of the *p*H value of the soil is essential and this may be followed by a determination of the "lime requirement." Finally, a measure should be obtained of the "exchangeable bases," upon which largely depends the continued reaction of the soil to fertilisers.

In general information about soils the following may be consulted:—Russell, *Soil Conditions and Plant Growth;* Hall, *The Soil.*

I. Sampling and Preparation for Analysis

Among the methods that have been used for obtaining samples of soil for examination in the laboratory the use of an auger has proved the most convenient.[1] In order to explore the subsoil and procure samples from any depth a screw auger alone is effective, but for ordinary analytical work a cylindrical auger is preferable. This consists of a cylinder of steel of about 1/16 in. in thickness, 12 in. long, and 2 in. in diameter, and it is easier to manipulate if it tapers slightly downwards. A slot ¾ in. broad extends down one side of the cylinder, and the edges of the slot and the bottom of the cylinder are filed down outside to a cutting edge. The top of the cylinder is fixed to a bar 2 feet in length, the top of which is fitted with a stout wooden cross handle. Having selected a site for sampling, a hole is first dug to lay bare the profile, in order to ascertain whether any special circumstances dictate the depth to which the sample of soil should be taken. In ordinary cultivated soils 9 in. is regarded as the conventional depth of the soil, the second 9 in. being regarded as the subsoil. But it may be found that the soil terminates abruptly before a depth of 9 in. is reached, or a "pan" may intervene. In such cases, and always in examining uncultivated soils, the thickness and depth of the layers to be sampled must be determined by the profile.

The surface is smoothed and the auger is thrust in with a twisting motion. If the soil is stiff and hard it may be necessary to go down a few inches only for the first cut, and then to remove the auger and extract the soil before replacing the auger in the same hole and continuing down to the 9-in. depth indicated by a mark on the outside of the cylinder. The contents of the cylinder are scraped out into a bag by the help of a chisel working

[1] See Russell, *J. Bd. Agric.*, 1916, **23**, 342.

through the slot in the side. The operation is repeated still in the same hole for the second 9 in. of subsoil. From six to ten borings should be taken at places scattered about the area in question and the samples mixed in order to get a composite representative sample.

At the laboratory the samples are turned out and spread, each on a tray or a sheet of glazed paper, on a table in an airy warm room. It facilitates drying if the surface is turned over from time to time and the lumps broken down by hand. The soil can be reduced to powder more readily before it is quite air-dry; at the right point it should be broken down in a mortar with a wooden pestle, so as not to break up the included stones. The powdered material is thrown on to a sieve with round holes 2 mm. in diameter. The stones retained by the sieve are weighed, washed to remove adhering earth, dried and weighed again. The nature of the stones should be recorded. The fine earth passing the sieve is again exposed and turned thoroughly air-dry, after which it is weighed (for comparison with the weight of stones) and is ready for analysis.

Determination of Moisture and Loss on Ignition.—As a preliminary to the determinations it is necessary to estimate the water retained by the air-dried soil and the loss on ignition, which includes the organic matter and the water of constitution of the clay and other hydrated silicates.

About 20 g. of air-dried soil is weighed out into a tared basin (platinum, vitreosil or porcelain) and dried off in an oven maintained at 105° for twenty-four hours. The basin and its contents must be allowed to cool in a desiccator before weighing. A definite figure of some value in characterising the soil, *hygroscopic moisture*, may be determined by allowing the soil to come into equilibrium in a chamber over sulphuric acid of 50 per cent. relative humidity (density, 1·3325 at 15°, to be obtained by adding 23·4 c.c. concentrated acid to 57 c.c. of water) weighing and then putting it into an atmosphere in contact with concentrated sulphuric acid. It is then reweighed and the difference gives the hygroscopic moisture.

The basin of oven-dried soil is now placed in a muffle and ignited for half an hour at a bright red heat, or it may be heated over a Bunsen burner with a sheet of platinum-foil above the soil. There may be some loss of weight through decomposition of calcium and magnesium carbonates. If the carbon dioxide evolved is determined separately, the amount may be subtracted from the total loss in order to get the true loss on ignition. Or the ignited soil may be moistened with a solution of ammonium carbonate, which is then dried off and finally removed by gentle ignition before weighing.

II. Mechanical Analysis

The aim of mechanical analysis is to separate the soil into a series of fractions, each consisting of the particles between certain limits of size. The size determines the velocity with which the particles fall through water. Particles below a given size can therefore be obtained by collecting whatever remains suspended for a given time in a column of water of given depth. Many methods of analysis have been employed. The original method of sedimentation in a beaker has now been generally replaced by the pipette method, which requires much less time and comparatively small bulks of liquid to separate. The method to be described has been adopted as the official method to be used in Great Britain, and is in conformity with the method recognised by the International Society of Soil Science. Further details may be found in *Agricultural Progress*, vol. v., 1928.

The operation is divided into two sections — dispersion and analysis.

It is necessary first to break up the temporary aggregates of the soil particles, due either to the cementing action of organic matter or the agglutination of soil colloids. Twenty g. of air-dried soil is weighed out into a 600 c.c. beaker, and covered with about 60 c.c. of 6 per cent. (20 volume) hydrogen peroxide. The solution is gently heated and stirred as the reaction proceeds. When much organic matter is present there is a violent reaction and the frothing must be watched. Further additions of peroxide are necessary until the reaction ceases and the soil loses its dark colour. Cool and add 150 to 200 c.c. $N/5$ hydrochloric acid, according to the amount of carbonates present. The contents are well stirred, allowed to stand and filtered through an 18 cm. hard filter-paper, the first turbid runnings being poured back. A filter pump may be used. Wash three times with 100 c.c. distilled water, taking care not to wash down the soil. If need be, continue the washings until they come through free from acid. The filter paper is now removed, spread on to a watch-glass, and the soil is washed with hot water on to a 2 mm. woven wire sieve held in the mouth of a beaker. Suitable sieves can be obtained to the specification of the Institution of Mining and Metallurgy, No. 70. After washing off the soil the filter paper should be rolled up and squeezed, wetted again, and squeezed until it yields no more turbid liquid. The material on the sieve is gently rubbed with the finger or a rubber pestle until clear of the finer fractions. It is then dried in the oven at 105° and weighed. (= *Coarse Sand.*)

The acid filtrate contains some dissolved material, calcium chloride from the carbonate, sesquioxides and silica. Precipitate the solution

with ammonia and ammonium carbonate, filter off and weigh the precipitate after gentle ignition. This gives an approximate figure for the *loss by solution.*

The sediment passing the sieve is now transferred to a shaking bottle of 1 litre capacity. Distilled water is added up to about 500 c.c. with 50 c.c. of 10 per cent. ammonia. The bottle is then placed in an end-over-end shaking machine run at 30 to 40 revolutions per minute, and is shaken, either until the next day in the case of sandy soils, or for a further whole day in that of heavy clay soils. The suspension is then poured into a measuring cylinder and made up to 1 litre with distilled water. A 20 c.c. pipette with a long tube is then passed through a cork large enough to rest on the mouth of the measuring cylinder and so adjusted that the point of the pipette will come to exactly 10 cm. below the surface of the liquid.

The contents of the cylinder are thoroughly shaken with repeated inversions for about a minute and the cylinder is then put on a level surface to stand for four minutes forty-eight seconds. A few seconds before the time is up the pipette, with the top closed, is carefully lowered into the liquid, opened at the exact time and filled slowly so as to avoid causing eddies in the bulk. The contents of the pipette are delivered into a tared 7 cm. porcelain dish, dried down on a water-bath and finished in the oven at 105°, allowed to cool in a desiccator and weighed. It is desirable also to determine the loss of weight on ignition. The number of mg. in the oven-dried material divided by 4 equals the sum of the percentages of *silt + clay* in the air-dried soil. The contents of the cylinder are again shaken for a minute and allowed to stand for eight hours before again drawing off 20 c.c. at 10 cm. below the surface, which will now be a little lower in the cylinder than before. The contents of the pipette are again drawn off and weighed as before, whereupon mg. divided by 4 equals percentage of *clay*. The percentage of silt is then obtained by subtracting this from the previous figure. Again determine the loss on ignition. The manipulation is made easier by a special pipette and stand which can be obtained from the instrument makers.

The cylinder still contains the fine sand. Pour away the bulk of the supernatant liquid and transfer the sediment to a 400 c.c. beaker. Make up with water to a depth of 10 cm., stir well and allow to stand for four minutes forty-eight seconds. Pour off the turbid suspension, fill up with water to the mark as before and repeat Continue until the water above the sediment is no longer turbid at the end of four minutes forty-eight seconds. The *fine sand* remaining in the beaker is then washed into a tared dish, dried at 105°, weighed, ignited and weighed again.

The results can now be assembled :—

(1) Moisture in air-dry soil.
(2) Loss by solution.
(3) Carbonates (separate determination).
(4) Coarse sand, 2·0 mm. to 0·2 mm.
(5) Fine sand, 0·2 mm. to 0·02 mm.
(6) Silt, 0·02 mm. to 0·002 mm.
(7) Clay, below 0·002 mm.

III. Chemical Analysis

The material for analysis is the fine earth passing the 2 mm. sieve and in an air-dry condition. The following determinations are usual :—

1. Nitrogen.—Ten to 20 g. of soil is weighed out and the nitrogen determined by the normal Kjeldahl process. No account need be taken of the small amount of nitrate present.

2. Soluble Mineral Constituents.—Twenty g. of soil is weighed out into a hard glass flask, covered with 70 c.c. concentrated hydrochloric acid and boiled for a short time to constant strength. The flask is then loosely stoppered, placed in the water-bath and the contents allowed to digest for about forty-eight hours with occasional shaking. The solution is cooled, diluted, filtered and made up to 250 c.c. In aliquot portions of this 10 per cent. solution the desired constituents are determined, *i.e.*, K_2O and P_2O_5, occasionally CaO, MgO, Fe_2O_3 and Mn_2O_3.

Potassium.—In the estimation of potash and phosphoric acid special care must be taken to eliminate silica. Fifty c.c. of the solution is evaporated to dryness in a porcelain basin with a little calcium carbonate (0·1 to 0·5 g.) and the residue is ignited. The charred mass is taken up with dilute hydrochloric acid, filtered, again evaporated to dryness and heated in the air-bath at 105° for half an hour. The residue is taken up with water, the solution filtered and then mixed with 25 c.c. of a solution of platinum chloride containing 0·005 g. of platinum per c.c. The mixture is gently evaporated on the water-bath to a magma and then washed on to a filter paper with a solution of ammonium chloride which has been saturated with the double chloride of platinum and ammonium. After this washing it is washed with alcohol and finally dissolved off the filter paper into a small tared basin, evaporated, dried and weighed. The perchlorate method of estimating the potash (see Vol. II., p. 404) may replace the platinum precipitation.[1]

Phosphoric Acid.—For the determination of the phosphoric acid the residue after the second evaporation and the solution of the potash

[1] *J. Agric. Sci.*, 1912, 5, 52.

is taken up with dilute sulphuric acid and made up to about 50 c.c. Five g. of ammonium nitrate is then added and 50 c.c. of a solution of ammonium molybdate containing 60 g. molybdic acid per litre. The mixture is put aside in a warm place for twenty-four hours, the precipitate filtered off and washed with ammonium nitrate solution. It may then be estimated either titrimetrically or dissolved by dilute ammonia into a tared basin, evaporated and gently ignited over an Argand burner, when it will contain 3·794 per cent. of P_2O_5.

3. **"Available" Phosphoric Acid and Potash.**—It has often been sought to distinguish between the total phosphoric acid and potash in a soil that may be extracted by strong hydrochloric acid, and the portion of these constituents which are in such a state of loose combination that they may be regarded as immediately available for the growing crop. It is recognised, for example, that most of the potash in the unweathered silicates to be found in the soil will come into solution with such slowness and difficulty that it is of no account as a fertiliser, *e.g.*, the ultimate analysis of a soil may show 2 or 3 per cent. of potash of which concentrated hydrochloric acid extracts only one-fifth or one-eighth. Phosphoric acid may also be present in very stable combination with iron. It was in consequence suggested that extraction with a weak acid would more nearly resemble the natural processes of solution and would select these combinations of these constituents which could be immediately utilised for crop production. Dyer suggested the use of a 1 per cent. solution of citric acid as approximating in composition to the root sap of the growing plant. It is now generally held that the solvent action of the roots is wholly due to the carbon dioxide they give off, and consequently a solution of carbon dioxide in water would probably correspond more closely to natural conditions. However, there is no sharp distinction in kind between the material that dissolves and that which remains insoluble, the eventual reaction is a balanced one depending upon the relative masses of the acid water and soil; and repeated extractions with acid of the same strength will still continue to dissolve phosphoric acid and potash. Consequently the determination must be treated as a conventional one to be interpreted empirically, and the citric acid solution is still employed because of the number of analyses that have already been made by that method.

The procedure by Dyer's method[1] is to place 200 g. of air-dried soil in a Winchester quart bottle with 20 g. citric acid and 2 litres of water. The bottle should have been well soaked in acid before use in order to extract any soluble potash. In Dyer's original process the mixture was allowed to stand for seven days with occasional shaking; an

[1] *J. Chem. Soc.*, 1894, **65**, 115.

equivalent result can be obtained by putting the bottle in an end-over-end shaker for twenty-four hours. The solution is then filtered off and two portions of 500 c.c. each are evaporated down for determinations of K_2O and P_2O_5, the same procedure being followed as has already been described. In the interpretation of results by this method it may roughly be considered that soils containing less than 0·01 per cent. of P_2O_5 require phosphatic fertilisers, the critical figure being higher for clayey than for sandy soils. A similar figure, 0·01 per cent. of K_2O, may be adequate for cereals but is insufficient for the full development of root crops.

4. Carbonates.—A number of methods are available for the determination of the amount of carbon dioxide evolved on treating the soil with dilute acid. This will in the main be derived from calcium carbonate, though occasionally magnesium carbonate may be present. In setting out results the carbon dioxide evolved is expressed as calcium carbonate. The choice of method is determined by the proportion of carbonate present, which may vary from 20 to 30 per cent. down to an infinitesimal amount. If there is visible effervescence on treating the soil with acid there is approximately more than 1 per cent., but the majority of soils which have not been artificially enriched contain less than this.

When the soil is rich in calcium carbonate a simple gravimetric method may be employed. For this estimation a small wide-mouthed flask is fitted with a stoppered funnel and an inlet tube leading to the bottom of the flask. The exit tube leads to two U-tubes containing calcium chloride and a weighed U-tube containing soda lime. A weighed portion of soil (10 to 20 g.) is placed in the flask, covered with water, then dilute hydrochloric acid is admitted little by little to avoid excessive effervescence until action ceases. The contents of the flask are then gently warmed and a current of air is drawn through in order to sweep out the carbon dioxide in the flask and in the solution. The soda-lime tube is then re-weighed to ascertain the amount of carbon dioxide absorbed.[1]

In soils containing but little calcium carbonate more accurate results can be obtained as follows:—Fifty g. of the soil is placed in a small flask furnished with a stoppered funnel and an inlet and exit tube. Air freed from carbon dioxide is drawn by means of a pump through the flask and into a small Reiset tower containing a known volume of normal sodium hydroxide solution, made from metallic sodium, so as to be free from iron, alumina, silica, etc. The soil is decomposed by hydrochloric acid, delivered through the stoppered funnel and the evolved carbon dioxide expelled by bringing the contents of the flask to a gentle boil while the air current is passing; the current is

[1] See also Collins, *J. Soc. Chem. Ind.*, 1906, **25**, 518.

continued until all the evolved gas has been swept forward. The carbon dioxide is absorbed in the Reiset tower and is determined by a double titration. Phenolphthalein is first added, and normal hydrochloric acid run in little by little with shaking until the pink colour is ready to disappear. The final disappearance of the pink colour is carefully brought about by the use of an *N*/10 hydrochloric acid solution; the volume of acid used up to this stage need not be recorded, as this forms only the starting-point for the titration proper, when the carbon dioxide is all combined as bicarbonate. Methyl orange is then added and the titration continued with an accurate *N*/10 hydrochloric acid solution until the colour change takes place. The hydrochloric acid used in this latter estimation is alone taken into account and is equivalent to the carbon dioxide set free from the state of bicarbonate. A blank titration must also be made of the sodium hydroxide solution used for the absorption and a correction made for any carbon dioxide contained.[1]

There are two opposing sources of error in the determination. The evolved carbon dioxide forms a supersaturated solution and is not readily shaken out even on boiling at reduced pressure. On the other hand, many soils, especially those rich in humus, will give off some carbon dioxide from the action of acid upon the organic matter at boiling temperatures.

5. **Nitrates.**—The nitrates should be determined on the freshly sampled undried soil which is rubbed through the 2 mm. sieve. If, however, the soil is in too wet and clayey a condition to permit of this, it may be dried by spreading in a thin layer in an oven at 50° to 55° for twenty-four hours. This, according to Russell, will add about two parts per million of nitric nitrogen. Two hundred and fifty g. of the soil is weighed out and loosely packed in a Buchner funnel, a second sample being taken for a determination of the water present in the soil. The soil on the filter is then moistened with hot distilled water, and when permeated the pump is started. Successive small quantities of hot water are then poured on, the leaching will usually have been completed when about 400 c.c. has passed through. The filtrate is made up to 500 c.c. and two portions of 200 c.c. are taken for analysis. The extract is boiled down to about half its bulk with a small quantity of ignited magnesia (about 0·05 g.), transferred to an 8 oz. bottle and acidified with acetic acid, taking care to dissolve the magnesia. In the bottle is placed a copper-zinc couple made by taking a strip of zinc foil, cleaning it in caustic soda and sulphuric acid and then immersing it for a few seconds in a 2 per cent. solution of copper sulphate. The bottle is then corked and incubated at 25° to 30° for two days. The ammonia is then distilled off with magnesia and

[1] See also Amos, *J. Agric. Sci.*, 1905, 1, 322; Marr, *ibid.*, 1909, 3, 155.

estimated by titration with $N/50$ sodium hydroxide, using methyl red as indicator, or by Nessler's process.

An alternative method of reduction by Devarda's alloy is described by Russell.[1]

Determination of Acidity (*p*H Value)

The state of the soil as regards acidity or alkalinity is one of the most important factors in determining the use of fertilisers and the need or otherwise for lime, the suitability of the soil for certain crops and the tendency of the soil to encourage particular diseases. For example, barley, swedes and lucerne fail on acid soils; oats and potatoes are resistant. "Finger-and-toe" is a disease of *Brassica* associated with acid soils; common potato "scab" is only troublesome on alkaline soils. Spurrey, sheep's sorrel and corn marigold are troublesome weeds on acid soils.

The determination of the reaction is not, however, a simple matter. The acids or acid-forming substances are weak, *e.g.* the complex organic acids (so-called humic acid) produced by the decay of vegetable matter; the soil solution in contact with the soil particles is strongly buffered by the calcium phosphates and the colloidal double silicates present; adsorption phenomena also intervene. The most valid determination that can be made is that of the hydrogen-ion concentration (usually expressed as the reciprocal of the logarithm of the hydrogen-ion concentration or *p*H value) but even that will vary with the amount of water present, the degree of dispersion of the soil particles, etc.[2] Direct determinations of the *p*H value by means of the hydrogen electrode can be made by the apparatus described by Crowther[3] or by means of the quinhydrone electrode described by Biilmann,[4] but as such elaborate apparatus is usually only available in a special soil laboratory the determination is usually made by indicators. A sensitive qualitative test is described by Crowther.[5] A few c.c. of a suspension of calcium carbonate in distilled water which has been boiled to expel carbon dioxide, is coloured with cresol red and poured on to a few grams of the air-dried soil. If acid, the colour is changed to yellow, but remains red if the soil is neutral or alkaline. This test cannot be used in the field because the carbon dioxide normally present in the soil will bring about the colour change.

Of wider application is the "B.D.H. Soil Testing Outfit," which now can be obtained from all dealers in chemicals. This consists of a porcelain dish with two communicating compartments, in one of which

[1] *Chemists' Year Book*, 1927, p. 806.
[2] See Fisher, *J. Agric. Sci.*, 1921, **11**, 19.
[3] *J. Agric. Sci.*, 1925, **15**, 201.
[4] *J. Agric. Sci.*, 1924, **14**, 232.
[5] *Loc. cit.*, p. 252.

a sample of the soil is placed and mixed with the indicator. The liquid is then drained off into the other compartment, where its colour can be seen. A mixed indicator is used which gives a range of colours from blue for an alkaline soil, though green and yellow to red for a strongly acid soil. Approximate *p*H values may be thus obtained, but for more accurate determinations the "B.D.H. Capillary Comparator" may be used.

For the determination, 20 g. of the air-dried soil is shaken with 100 c.c. of distilled water for one hour in an end-over-end shaker. The bottle may then be put aside to settle for twenty-four hours or may at once be centrifuged; a slight turbidity or yellowness is of small account with the capillary tube method. Filtration will give a clearer liquid, but itself introduces a small change in the *p*H value. A measured quantity of the fluid is then drawn off into a watch-glass by the capillary pipette provided and mixed with an equal volume of the indicator. The range of indicators provided which covers soils is as follows:—

Brom-phenol blue	*p*H 2·8 to 4·6
Brom-cresol green	„ 3·6 „ 5·2
Brom-cresol purple	„ 5·2 „ 6·8
Brom-thymol blue	„ 6·0 „ 7·6
Cresol red	„ 7·2 „ 8·8

The coloured mixture thus obtained is drawn into one of the capillary tubes and matched against the corresponding indicator card. Further mixtures are made of the soil solution with other indicators until a tint has been matched to give the required *p*H value. More accurate estimations may be made with the Heilige Comparator[1] or by Fisher's method (*loc. cit.*)

Lime Requirement

The determination of the *p*H value of a soil gives reliable information as to the necessity or otherwise of applications of lime either as caustic lime or carbonate, information such as could not be obtained from the determination of the amount of carbonate present. Many soils show only a trace or even no carbonate, yet they possess a neutral reaction and show no response to dressings of lime. This is due to the fact that the soil particles, and particularly the soil colloids, are saturated or nearly saturated with replaceable calcium and other bases and so supply the bases required for interchange with fertilisers and bacterial action. If a soil has a *p*H value of 6 or upwards, and is well supplied with replaceable calcium, it is unlikely to require any applications of lime unless the course of cropping and the use of fertilisers

[1] See Crowther, *Chemists' Year Book*, 1928.

is such as to make considerable demands upon the bases. When, however, the *p*H value falls below 6 and the soil begins to reveal a shortage of base, liming will be desirable and it becomes important to ascertain what quantity is likely to be required. The method usually followed is that of Hutchinson and MacLennan,[1] which depends upon the absorption of calcium from a solution of its bicarbonate. A saturated solution is prepared by placing 10 g. of finely-divided calcium carbonate with distilled water in a sparklet bottle. After liberation of the gas the bottle is shaken occasionally for about twenty minutes, the solution is poured off, diluted with one-third its volume of distilled water and filtered, when it will be approximately *N*/50. A weighed quantity, about 20 g., of air-dried soil is placed in a litre bottle, the air is displaced by carbon dioxide and 300 c.c. of bicarbonate solution is added. The bottle is placed in a shaking machine and agitated for three hours, then filtered and 150 c.c. of the filtrate taken for titration with *N*/10 acid, using methyl orange as an indicator. Meantime a similar portion of the original dilute bicarbonate solution is titrated. The difference between the two results represents half the calcium carbonate absorbed by the soil, 1 c.c. of *N*/10 acid = 5 mg. $CaCO_3$. The "lime requirement," *i.e.* calcium carbonate required to bring the soil to the neutral point, can then be calculated; on the assumption that an acre-9 in. of the soil weighs approximately $2\frac{3}{4}$ million pounds each 0·1 per cent. of calcium carbonate required will be equivalent to 1 ton per acre. Critical studies of the method have shown that it does not give absolute results. With heavy soils the result will to some degree depend on the dispersion effected; again, with soils very rich in organic matter the amounts indicated are excessive, since the soil may be healthy long before it becomes saturated with calcium. But with ordinary soils the "lime requirement" thus estimated provides a useful figure.

Exchangeable Bases

The work of Way, Gedroiz, Hissink and others has shown that the texture of a soil containing an average proportion of clay is largely determined by the nature of the bases present in the double silicates of the colloidal particles. If sodium predominates, the clay is wet and sticky because of the gelatinous highly dispersed nature of the sodium salt. In the potassium and magnesium clays these properties are less pronounced; the calcium clay is comparatively dry and easily flocculated. When soils are in contact with solutions of these metals, the bases will be exchanged, the order of replacement being $Na > K > Mg > Ca$. If, for example, a soil is flooded with sea-water

[1] *J. Agric. Sci.*, 1915, 7, 75.

for some time the calcium becomes largely replaced by sodium and magnesium, and the soil becomes difficult to cultivate.[1] In normal clay soils the relation of bivalent to univalent bases (equivalents) should be 8 to 1 or above; at almost 5 to 1 the texture begins to deteriorate perceptibly. If calcium and sodium alone are determined, as the dominating constituents, the ratio by weight of CaO to Na_2O should be not less than 8.

In the determination of replaceable bases the method of Hissink[2] is adopted. Fifty g. of the air-dried soil are placed in a beaker with 200 c.c. of normal ammonium chloride solution warmed to 50° to 60°, and stirred for about two hours. The material is then left to stand overnight, when the supernatant liquid is poured off and filtered through a Buchner funnel as clear as possible. The soil in the beaker is again extracted with 200 c.c. of fresh ammonium chloride solution, stirring for half an hour at room temperature, allowed to stand, decanted and filtered as before. The process is repeated with successive quantities of 100 c.c. of solution until finally the soil is washed on to a filter and the leaching completed to make the bulk of the liquid up to 1 litre. The soil is then washed back into the beaker and the process repeated until a second litre of leachings is obtained. 500 c.c of the first filtrate is then taken for analysis and boiled down. As the concentration increases, probably some fine suspended matter that has passed the filter will become flocculated and should be removed by filtration. When reduced to a small bulk, the ammonium chloride is destroyed by boiling with strong nitric acid, and in the resulting solution the four bases, or calcium and sodium only, are determined by the usual methods, after removal of iron, aluminium and silica. The determinations are made on the second litre of leachings separately, and the amounts obtained are deducted from those given by the first filtrate.

An approximate figure of 0·3 per cent. CaO may be taken as indicating that the soil is adequately supplied with replaceable lime, but the value can only be interpreted in relation to the *p*H value and the amount of clay in the soil. As a rule the determination of exchangeable calcium is only required if the soil is devoid of calcium carbonate. If, however, such a determination should be required in the presence of calcium carbonate, ammonium chloride cannot be employed because of its action on the calcium carbonate, and it must be replaced by a normal solution of sodium chloride.

[1] Page and Williams, *J. Agric. Sci.*, 1926, **16**, 551.
[2] *Internat. Mitt. Bodenkunde*, 1922, **12**, 81; *Soil Science*, 1923, **15**, 271.

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AIR

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THE composition of the air is remarkably constant, a fact which is sufficiently explained by the great turbulence of the atmosphere, its antiquity and the great diffusibility of gases.

Until the closing years of the nineteenth century it was believed that there was nothing more to know about the gaseous constituents of air—nitrogen, oxygen and a small and somewhat variable proportion of carbon dioxide, with possibly traces of other well-known gases. The discovery of a new dense gas in air by Rayleigh and Ramsay was but the prelude to the separation and characterisation of a new group of inert, monatomic gases which had been ignored since Henry Cavendish made his classical researches on the atmosphere.

The percentage composition of dry air is given by Kaye and Laby [1] on the authority of Sir W. Ramsay and G. Claude as follows:—

	Nitrogen.	Oxygen.	Argon.	Carbon dioxide.	Krypton.	Xenon.	Neon.	Helium.
Weight . .	75·5	23·2	1·3	0·046 to 0·4	0·028	0·005	$0{\cdot}0_3 86$	$0{\cdot}0_4 56$
Volume . .	78·05	21·0*	0·95	0·03 to 0·3	...	...	$0{\cdot}0_2 123$	$0{\cdot}0_3 40$

* 20·91 according to Kreusler.

Besides the constituents above indicated, air always contains water vapour, varying in amount with its temperature and recent association with water. Other gaseous constituents which may be considered normal in the minute amounts in which they are usually found or thought to be found are ozone, hydrogen peroxide, nitrous acid, ammonia, marsh gas and hydrogen.

The interest of the analyst in air is not usually in the proportion of its main constituents although their determination may sometimes be necessary, but rather in those constituents the amounts of which are, theoretically at least, controllable. Nevertheless, in examining the air of confined spaces it is useful to be certain that there is no gross abnormality in the proportion of the major constituents. One of us, for example, found that the air of a cold storage, where difficulty

[1] *Physical and Chemical Constants*, 1918, p. 125.

was found in keeping candles alight early in the morning when the locally generated electric light was not available, was deficient in oxygen to the extent of about 4 per cent. This was apparently due to compressed air from a tunnel, which was being bored beneath the river close to the storage, finding its way in through a subsoil, containing pyrites or ferrous iron, and a disused well. The failure of combustion was due to an excess of nitrogen, not to carbon dioxide.[1]

When the atmosphere is considered as a whole, ozone is probably the most important of these minor constituents—not as the life-giving gas popularly supposed to be present in large amounts in the air of most health resorts, but rather by reason of its power of absorbing and cutting off from the earth's crust a band of ultra-violet rays of wave-length less than 2900 Å.U. Ammonia, methane and hydrogen are the products of some forms of decay of organic matter.

Besides these gases and vapours, air contains both liquid and solid particles—droplets of water, frequently containing dissolved matters, and dust particles which, once caught up into it by eddies or projected from volcanoes or chimney shafts, are by reason of their small size so long in falling that they may be considered as part of the air.

The concentrated human activities of towns and even of villages give rise to a variety of abnormal constituents, oxides and acids of sulphur, sooty and tarry particles from products of the more or less complete combustion of fuel and other acid and "chemical" fumes, whilst the internal combustion engine is responsible for a certain amount of carbon monoxide in addition to other products of combustion.

I.—Determination of the Gaseous Constituents of Air

1. Oxygen

Oxygen is the one constituent of air which can be determined with precision by the ordinary methods of gas analysis. It can be absorbed by alkaline pyrogallate or, from air or gases less rich in oxygen, by phosphorus or by chromous chloride. Pyrogallate is most commonly used. Oxygen can also be absorbed at elevated temperatures by copper or other metals.

The usual methods of gas analysis are described in the section of this work devoted to that subject (*cf.* Vol. I., pp. 245, 301). It may be useful here to refer to methods which have been used when great accuracy was desired.

A very good discussion of this matter will be found in a paper by H. E. Watson,[2] who worked with P. A. Guye on the oxygen content of the upper air. Dumas and Boussingault had employed absorption by heated copper, which was slow and complicated. Leduc used a

[1] *Cf.* B. Blount, *Analyst*, 1906, **31**, 144. [2] *J. Chem. Soc.*, 1911, **99**, 1460.

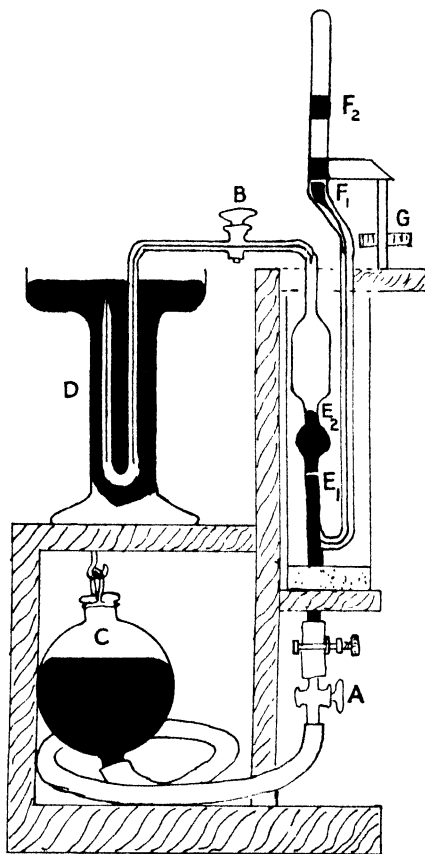
gravimetric method with cold phosphorus as an absorbent which was also slow. Regnault and later Bunsen had used explosion with hydrogen. Watson used heated phosphorus and measured the air dry and free from carbon dioxide. This method has been simplified by Aston whose technique is here described.

Aston's Method for Oxygen.[1]

The advantage of absorption of oxygen by phosphorus instead of pyrogallate methods is the certainty that the reagent introduces no gas or vapour into the unabsorbed gas. Further, by working with *dry* gas the precision of measurement is greater than is possible when the gas burette is moist. Phosphorus can only be used, however, when the gas is free, as air usually would be, from hydrocarbon vapours which somewhat interfere with the accuracy of the absorption. Aston has described a useful differential method.

FIG. 87.

The samples to be analysed are transferred to test-tubes, holding rather more than is required for an analysis (Aston used about 10 c.c.), into the closed ends of which has been fused a little potassium hydroxide. Here they remain over mercury for at least two hours before analysis in order to remove carbon dioxide and water vapour.

The measuring burette and barometer tube (Fig. 87) are normally kept full of mercury with the stopcock A turned on to avoid fracture by expansion. In order to perform an analysis, the capillary stopcock B is closed and the reservoir C lowered until the level of the mercury in the barometer tube is a little below its upper and broader part. The stopcock A is then closed, and the sample tube held down over the inverted syphon tube in the mercury trough D. When the capillary stopcock B is now opened, the air flows into the upper part of the burette and the mercury rises again to the top of the barometer

[1] *J. Chem. Soc.*, 1919, **115**, 472.

tube; in order to prevent this happening with destructive violence, the lower part of the barometer is made of capillary bore (less than 2 mm.). After waiting for a few moments for pressure and temperature to adjust themselves the sample tube is raised, flooding the end of the inverted syphon with mercury, the stopcock A is opened again, and by lowering the reservoir, mercury is caused to flow through the syphon and fill the capillary tube when B is turned off.

It will be seen that the volume of air introduced in this way is constant, being the volume of the upper part of the barometer tube (in Aston's apparatus a little less than 10 c.c.); the pressure being atmospheric plus the small difference of level between the top of the syphon tube and the mercury in the trough, the quantity will also be approximately constant. This quantity is now accurately measured by adjusting the mercury level in the burette exactly to the lower fixed reading point E_1; this can be done with the greatest nicety by bringing the mercury nearly up to the mark by manipulation of the reservoir and stopcock, and finally (with the latter closed), squeezing the short length of rubber pressure tubing with the screw clip provided as indicated. The volumes of the burette and barometer are such that the surface of the mercury in the latter will be somewhat as indicated in the diagram, and the lower movable reading point, F_1, may be exactly adjusted to it by means of the micrometer screw G. The barometer and the parts of the burette where readings are taken are all made of the same piece of glass tube, 0·9 cm. in internal diameter, to eliminate meniscus error. The reading points are all sleeves of brass tube 1 cm. long fitting the glass tubes, the fixed ones clamped, the moving ones sliding loosely. The readings of the micrometer having been taken, the air is now forced into the laboratory tube. This is a quartz test-tube holding rather more than 10 c.c., to the top of which (not quite in the centre) has been fused a pellet of phosphorus. These pellets may be easily made by allowing melted phosphorus to flow from a pipette with a narrow mouth into a tall cylinder of cold water. One spherule of about 2 to 3 mm. in diameter should be ample, and this is introduced into the inverted quartz tube full of mercury, shaken into position and fused into the side with a touch from a Bunsen flame. When all the air has been transferred from the burette to the quartz tube, the phosphorus is inflamed and then heated to boiling-point in order to ensure the complete removal of all oxygen. Some time is allowed for the phosphoric oxide to settle, when the deoxidised air is drawn back into the burette. It was feared when the apparatus was designed that it might be difficult or even impossible to perform this operation satisfactorily as small bubbles of air were expected to remain behind on the walls of the quartz tube, now of necessity contaminated with the products of combustion.

Such bubbles are formed, but they can be dislodged by touching with the syphon tube and then washed with a little mercury into the burette.

The residue is measured at such a volume that if the air is normal the two pressures measured would be identical, so that a very small difference of pressure only need be determined. For this purpose the upper fixed reading point, E_2, is used, this being set once for all during the construction of the burette, so that the upper part of the burette holds exactly 79·0 per cent. of the whole. The upper movable reading point, F_2, is also soldered to the sliding carrier at exactly the same height above the lower one as that between the fixed points. Hence it will be seen at once that for normal air the mercury at the measurement of the residue should stand at the upper movable reading point, or if the dimensions of the apparatus are not quite correct, at a constant small distance above or below it, a correction easily determined at any time by an analysis of normal air. If, on the other hand, there is reduction in the percentage of oxygen present, the mercury will stand at a higher level, the difference being measured on the micrometer.

A decrease of oxygen from 21 per cent. to 20 per cent. corresponds with a change in height of mercury in the ratio of 79 to 80; as the normal difference between the fixed and movable reading points in the apparatus in use (by Aston) is 237 mm., this gives exactly 3 mm. per 1 per cent. change. The micrometer has a range of 10 mm., which is more than ample for the changes expected, and analyses should be consistent to well within 0·1 per cent. on total air, the head of the micrometer being divided into twentieths of a millimetre corresponding with one-sixtieth per cent.

The use of phosphorus as an absorbent is, of course, not confined to an apparatus of Aston's type; moist phosphorus can conveniently be used in a Hempel pipette and dry phosphorus is suitable with any apparatus having the inverted syphon arrangement used by Aston. This device was used by Sir William Ramsay in much of his work with gases and seems first to have been used by Dittmar. It is very convenient; in our opinion, much more so than the "laboratory vessel" used by Frankland, MacLeod, Thomas, and Bone and Wheeler. Aston's ingenious comparison method would be well worth adopting if one had a great many air analyses to do, and could be applied in a modified way to any apparatus in which two divisions represented volumes of approximately 1 and 0·79 respectively. It would probably be inadvisable to use phosphorus as an absorbent of oxygen in the presence of any combustible gases as some of these would almost certainly be burned with the phosphorus. If a very exact determination of oxygen were required in such mixtures, chromous chloride would seem to be the safest reagent to use.

2. Carbon Dioxide.

Carbon dioxide is a product of the respiration of animals and, to a less extent, of plants. It is a principal product of all combustion. Notwithstanding this enormous production, the proportion in the air varies only within very narrow limits. It tends to decrease below 0·03 per cent. of the volume of the air in mountainous and uninhabited districts and only rises appreciably above this in towns, or the neighbourhood of great fuel-using works. This almost unvarying proportion is maintained by two great agencies of nature—the growth of green plants, which obtain their carbon by photosynthesis from the carbon dioxide of the air, and the carbonate-bicarbonate buffer system in the ocean. Thus the air all over the globe is brought in contact with a system which will absorb carbon dioxide, with this difference, that whereas vegetation on land almost entirely acts as an absorber of carbon dioxide, the sea is rather an equaliser, since it will either yield that gas to or take it up from air according as the air contains less or more than the normal proportion.

Having regard to these facts, amounts of carbon dioxide much greater than 0·03 per cent. must be attributed to special local conditions—excessive production or insufficient removal of that gas; *i.e.*, to overcrowding or defective ventilation. Hence great importance has been attached to the determination of this gas.

Determination of Carbon Dioxide.

As an acid gas, carbon dioxide can be determined by absorption by alkalis. This may be done either by passing a rather large volume of air through a suitable absorbing train which will first remove dust and water vapour, and then through tubes or bulbs, previously weighed, containing the alkaline absorbent, which are again weighed after the experiment; or by agitating a known volume of air in a closed vessel with a small measured volume of standard alkali. The proportion of this gas in air is so small that if the third alternative, a gasometric method, is to be used, very special precautions must be taken, as small variations of either temperature or pressure might easily affect the order of magnitude of the result.

When it is desired to ascertain the average proportion of carbon dioxide in air over a period, the gravimetric method has great advantages. It was used for this purpose by the late J. Parry Laws in his work on sewer air. The following details sufficiently describe the process. It is obvious that they may be modified according to the needs of the case or the taste of the worker.

A. Gravimetric Method.—This method necessitates the drying of the air before it passes over the absorbent for carbon dioxide. It

can therefore be advantageously combined with the determination of water vapour, and was so used by Parry Laws and by Haldane and Pembry. The apparatus is extremely simple; the air, which may be freed from dust, if necessary, by passing through a *small* plug of cotton wool (a large one might appreciably affect the humidity of the air) is passed through a large U-tube or its equivalent filled with purified pumice moistened with strong sulphuric acid and then through a similar tube of which the first half is filled with soda lime, or if preferred one of the newer proprietary absorbents which are coloured to show when they will absorb no more. The second half of the tube is filled with an absorbent of water. If an ordinary U-tube is used, this must be calcium chloride; but if the two limbs are separated, sulphuric acid-pumice, which is better, may be used. Both tubes are weighed before and after the determined volume of air is passed through them. The whole arrangement may be fitted in a box which protects the tubes both from fracture and, in work in a public place, from the unwelcome attention of interested onlookers. Very great care is necessary in weighing the tubes. It is best to have two sets of tubes and to determine not actual weights but the difference of weight between similar pairs of tubes. This should be done after carefully wiping the tubes with a cloth which has been kept in the same room as the balance. The wiped tubes should be placed in or near the balance case and allowed to stand for half an hour before weighing to bring the surface of the glass in equilibrium with the air. The tubes may now be lifted by their wire suspensions and hung on the hooks of the balance, the absorption tube on one side (the left) and the "dummy," which it is convenient to have the lighter of the two, on the right. The difference of weight should be determined to 0·1 mg. The tubes are now connected with one another and with the aspirator which is to be used for drawing over the desired volume of air. If, as is usually the case, this is a vessel of water, a drying tube containing either sulphuric acid or calcium chloride must be interposed between the carbon dioxide absorbing tube and the water vessel. Since the percentage of carbon dioxide may be as low as 0·03 in pure air and 1 c.c. of carbon dioxide weighs approximately 2 mg., not less than 10 litres of air should be used for a determination if weighings are made only to 0·1 mg. If a micro balance weighing with precision to 0·01 mg. or less is used, a smaller volume may be taken, but lighter absorption tubes must then be used. Forms of U-tubes and other absorption apparatus which are suitable are shown in Figs. 88 and 89. (Fig. 89 is drawn from one of Parry Laws's open tubes.) If tubes like these are chosen, they should be weighed without the plugged rubber stoppers, which must be removed from both sets—absorption tubes and counterpoises—before putting them

in the balance case. The one thing to remember is to treat both sets in exactly the same way except that one set is used for absorption and the other is retained for comparison only. The recent history of the two sets for about half an hour before weighing *must be the same.* Haldane states that the maximum error of weighing counterpoised tubes is about 0·3 mg. In an example given by him, 30 litres of air were used for a determination. This is rather more than a cubic foot and would mean fifteen fillings of a two-litre aspirator, which is not very convenient. Parry Laws used a reversing aspirator which is still in one of our laboratories and is a convenient instrument, inasmuch as it needs no refilling but mere inversion. It is also reasonably portable.

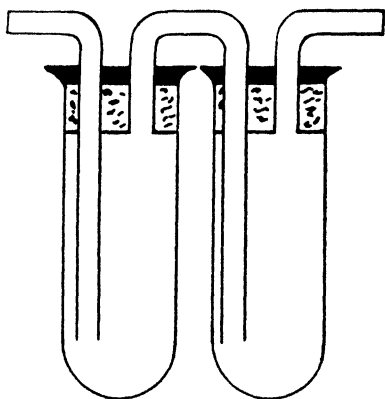
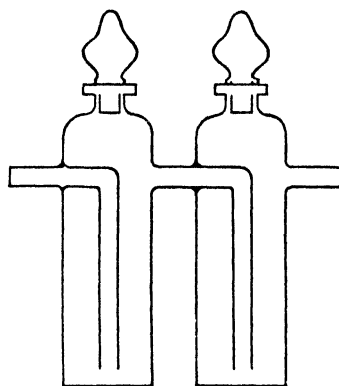



Fig. 88. Fig. 89.

B. Gas-volumetric Methods.—Various gas-volumetric methods have been proposed for the determination of carbon dioxide in air. Of these, the most convenient is that proposed by J. S. Haldane, which by a very ingenious means avoids the difficulty caused by slight alterations of temperature and pressure, which, while insignificant when constituents present in fair quantity are to be determined, are sufficient very seriously to affect the determination of a constituent present in so small an amount as 0·1 per cent. or less. This is done by bringing the volume of air operated upon under the same conditions of temperature and pressure as an approximately equal volume of air which is confined in a vessel within the same water-jacket. The required delicacy of measurement is obtained by having a bulb-form gas burette with a narrow graduated extension and effecting the final adjustment of pressure by means of a column of the potash solution which is used for absorption. The advantages of the apparatus are most apparent when it is necessary to make a great many analyses during a relatively short period. If it is left unused for long there is a great tendency for taps

to stick and also for the operator to lose skill in manipulating the rather delicate instrument. The great advantages of mercury as a confining liquid are bought at the expense of a rigid and sensitive routine.

Haldane's apparatus[1] is shown in Fig. 90. It consists of a measuring burette A, connected by a three-way tap B to the absorption pipette C, and attached at the bottom to the pressure bulb D, which is suspended from the hook of the rack and pinion E. The absorption pipette is connected by a T-piece to the levelling bulb F, and to the

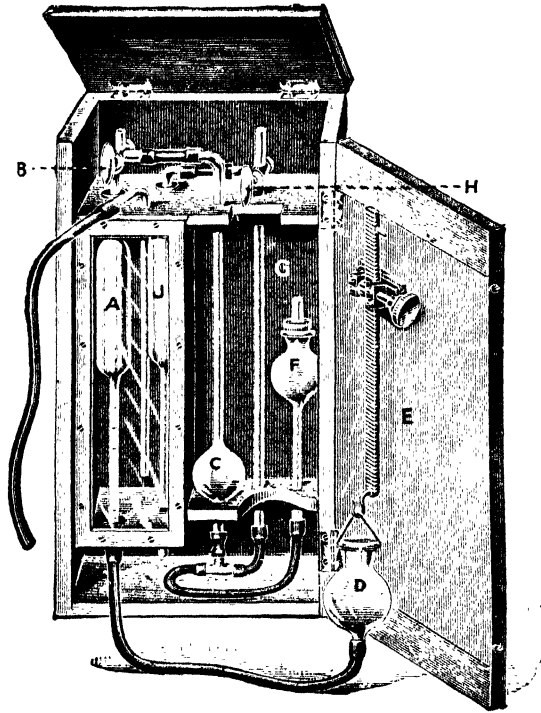



Fig. 90.

tube G, which is provided with a three-way tap H, at the top; the tap communicates through the connections shown with the control tube J. A and J are enclosed in a rectangular water-jacket which is provided with a glass tube, through which air is blown for thoroughly mixing the contents. The measuring burette A has a capacity of about 20 c.c.; the wide upper portion is ungraduated. The narrow lower portion, which is about 10 cm. in length, is divided into about 100 divisions, each of which corresponds to $\frac{1}{10,000}$ part of the capacity of the burette; the lowest division is marked 0, and the readings thus give parts per

[1] *Ventilation of Factories and Workshops.* First Report of Departmental Committee. Blue Book [Cd. 1302], 1903, Appendix.

10,000 directly. The tube of the absorption pipette C and the tube G are provided with levelling marks for adjusting the pressure. The whole apparatus is fitted in a portable case, the internal dimensions of which are $6\frac{1}{2} \times 12 \times 2\frac{1}{2}$ inches, and weighs about 5 pounds when charged ready for use.

The pressure bulb D is filled with mercury, which is used as the confining liquid; the absorption pipette is charged with a 10 per cent. solution of potassium or sodium hydroxide. In order to have a sharp index of the pressure under which the air is measured, the level of the solution in the narrow bore tube of the absorption pipette is taken as the index of pressure, instead of that of the mercury; the volume is adjusted to the level of the mark on this tube before and after the absorption of the carbon dioxide by raising or lowering D. The volume of air in the control tube J is adjusted before each determination by first putting it into communication with the outside air by momentarily opening the tap H, then connecting it with G, and adjusting the level of the solution to the mark by means of the bulb F which slides easily through a loosely-fitting cork or clip. A similar adjustment is made after the absorption, so that any change of volume due to an alteration in temperature or pressure is compensated. The water in the water-jacket must be thoroughly mixed before each adjustment. To obviate error due to variations in the moisture in the air, sufficient water is introduced into both the burette and the control tube to leave a little visible moisture inside each.

To make a determination, the air in the burette A is expelled by raising D and the sample of air for analysis drawn in, so as nearly to reach the zero mark of the burette, by lowering D; B is then opened so as to put A into communication with C, the control tube adjusted as described, and the reading taken, after adjusting to the mark on the tube C by raising or lowering D. The air is then driven over into C by raising the pressure bulb, and passed backwards and forwards two or three times; after finally passing back the air into the burette, the volume is adjusted as before and the reading taken. The whole estimation occupies about four minutes. The results may be relied upon to within 0·5 volumes per 10,000, after some experience with the apparatus.

It is necessary to ascertain by calibration or other appropriate means that the apparatus is well graduated. When it is desired to examine collected samples contained in bottles, an additional 3-way tap may be connected by rubber pressure tubing to the inlet of B so that a delivery tube filled with mercury can be inserted into the bottle of air, which is inverted and opened in a deep mercury trough. A form of apparatus with a cylindrical water-jacket, which possesses some advantages over the earlier pattern, is described by Haldane in

Methods of Air Analysis, 1918. This apparatus is specially useful in systematic work, involving many determinations in fairly rapid succession. When seldom used, the need of re-learning the technique is a disadvantage.

Pettenkofer's Method. The volumetric method associated with the name of Pettenkofer is convenient, fairly exact and rapid. The alkali used is baryta or lime, the reason being that the relative insolubility of their carbonates simplifies the final titration. Pettenkofer used oxalic acid for this titration but the use of this acid in alkalimetry is now for good reasons obsolete; it is more convenient to use hydrochloric acid. As to the alkali, it is usual, following Pettenkofer to use baryta, but lime water is equally suitable. Water at 0° dissolves 0·13 g. calcium oxide or 1·5 g. barium oxide per 100 c.c., forming solutions which are respectively 0·046 N and 0·20 N. The carbonates are about equally soluble—about 0·002 g. per 100 c.c. water, corresponding to 0·4 and 0·8 mg. of carbon dioxide respectively. The error in an actual experiment in either case is less than the solubility of the carbonates would seem to imply, as the presence in solution of $Ca^{\cdot\cdot}$ or $Ba^{\cdot\cdot}$ ions reduces the amount of carbonate dissolved. The fact that lime water is a more dilute alkaline solution than baryta water is against it, in that more solution has to be used in a determination, but on the other hand the action on the glass walls of the bottle in which the determination is carried out is likely to be less. Letts and Blake[1] have shown that this action on the glass is the principal error in the process.

It is unnecessary to use very large bottles for this determination. One litre of ordinary air contains about 0·3 c.c. of carbon dioxide which corresponds to 0·53 c.c. $N/20$ acid. The analyst can decide from his knowledge of his own capacity for delicate work and the special needs of the case what sized bottle to use. A two-litre bottle is not unduly large to handle, and on the other hand if a large number of results of a fair order of accuracy is desired smaller amounts can successfully be used.

Those who, for any special reason, desire to obtain results of very great precision would do well to consult the paper by Letts and Blake referred to.[2] This is a classic, full of historical information, and containing clear directions for working. When, as is usually the case, it is only desired to obtain a fairly exact determination for gauging the efficiency of ventilation of a room or building, the following method of working will be found convenient.

A sufficient number of clear glass bottles, each holding from one to two litres, is provided. These are cleaned and dried and, if desired,

[1] *Proc. Chem. Soc.*, 1896, p. 192.

[2] *Sci. Proc. Roy. Dub. Soc.*, 9 N.S., II., No. 15, p. 117.

the lower part of each is coated internally with paraffin wax as follows: "Ordinary white paraffin wax is melted and allowed to cool until near its solidifying point. It is then poured into the *cold* vessel, and the latter rolled round until a uniform and sufficiently thick coating is obtained over all parts. A little practice is necessary to effect this properly, but the operation is not difficult" (Letts and Blake). It will be sufficient to coat only the lower part of the bottle, as the upper part must be left sufficiently transparent for the titration of the residual alkali to be done in the vessel. The coated vessels must be allowed to stand, say, overnight for the paraffin to reach a stable condition, or it may crack when their volumes are determined. This is done either by adding measured volumes from a flask or flasks graduated for delivery, and then, as the vessel is nearly full, from a graduated cylinder or a burette, or the tared vessel may be filled with water and re-weighed. The volume up to the level in the neck, which the stopper or cork to be used will reach, should be taken, not the total volume to the top of the neck.

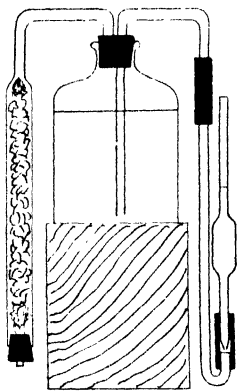



Fig. 91.

Vaselined glass stoppers may be used, or well-fitting rubber stoppers or paraffined corks may be found more convenient. The latter may usefully be bored with two holes which may be fitted with glass plugs for some work, or with a long and a short tube respectively, when it may be desired to draw a sample of gas from a confined or unenterable place. Some allowance should be made in this case for the volume of the glass of the tubes (10 g. glass = 4 c.c.).

The alkaline solution (lime- or baryta-water) is prepared by making a saturated stock solution with a good excess of the solid hydroxide and filtering off into a small bottle which will hold enough for immediate requirements and which has preferably been coated with paraffin as already described. This bottle (Fig. 91) should be fitted with a soda lime tube and a delivery tube with spring clip, capillary rubber end and a terminal glass plug. This arrangement is convenient for filling a pipette with the liquid in the manner shown, which is self-explanatory. It is a good plan to tint the alkali with phenolphthalein, which is the indicator used, so that, if in making a test an insufficient amount is added at first, a further quantity may be introduced as soon as the disappearance of the pink colour is observed. For a two-litre bottle 10 c.c. of lime water should yield a sufficient excess. Before a series of determinations is started the strength of the alkali should be ascertained by delivering 10 c.c. into a small narrow-necked flask from the same pipette as will be used in the determinations,

and titrating with $N/10$ or $N/20$ hydrochloric acid, taking great care not to breathe into the flask. It is a good precaution to interpose a plate of glass in front of the apparatus, that is between it and the operator, so as to deflect the breath, or, what is perhaps simpler, to cover the flask with a cardboard slip having a small central hole through which the jet of the burette may pass.

A narrow, well-graduated burette, which need not be larger than 10 or 20 c.c., with a fine long jet should be used. A N.P.L. certified burette will suffice. It is as well to make a second titration of a further 10 c.c. of alkali in the same flask without displacing the liquid remaining in it, in case the carbon dioxide of the air in the flask may have affected the first titration. The two results should not differ appreciably.

A determination may now be made. The selected bottle, which must be perfectly clean and dry, is opened in the atmosphere which is to be sampled and a glass or rubber tube introduced, reaching to the bottom. This is connected to an exhaust, which may conveniently be a syringe or rubber pump with appropriately fitted valves, and an amount of air at least five times the volume of the reaction bottle is drawn through it. If it is not convenient to bring the bottle into the air to be sampled, the double-bored stopper with tubes is used and one tube led into the air space, *e.g.* threaded through the keyhole of a manhole. If the length of tubing needed is considerable, small "compo" piping, which is cheap and easily obtainable, should be used, as rubber is likely to affect the composition of gas passing through it The other tube is connected to the exhaust, which is worked as before. During this operation a thermometer and aneroid barometer should be exposed near the bottle. When the sample is collected 10 c.c. of alkali is added and the stopper or the caps for the tubes replaced. The barometer and thermometer are read and noted with the other relevant details as to place, time, etc., and the liquid in the bottle is swung round so as to expose as large a surface for absorption of the carbon dioxide as possible; if the pink colour disappears a further volume of alkali is added and this addition noted (in the event of an accident this gives a useful minimum value for the CO_2 content).

After addition of the alkali sufficient time—some hours—must be allowed for complete absorption of the carbon dioxide. This process can be accelerated by swirling the lime- or baryta-water around the bottle. When ready for titration the stopper should be removed, any necessary washing of stopper or tubes done quickly with a minimum amount of recently boiled distilled water, or with distilled water through which CO_2-free air has been drawn (a soda lime tube can be attached by a rubber tube to the jet of the wash-bottle and the mouth-piece attached to a filter pump). Blowing with the mouth should not

be resorted to in washing the fittings. The alkali in the bottle is then quickly titrated with $N/10$ or $N/20$ HCl, using the precautions already suggested to avoid entry of air containing CO_2.

The following record of an actual determination will show the working:—

Carbon dioxide in air of laboratory at 13 hours (*i.e.* 1 p.m.), 22.2.29.
Air taken = 2580 − 10 c.c. = 2570 c.c. Temp. 21·6°. Bar. 762 mm.
Air at N.T.P. = 2388 c.c.
10 c.c. lime water = 8·94 c.c. $N/20$.
Residual alkali = 6·04 c.c. $N/20$.

required for CO_2 = 2·90 (1 c.c. $N/20$ = 0·56 c.c. CO_2 at N.T.P.)
2·90 × 0·56 = 1·62 c.c. 1·62 × 100/2388 = 0·068 per cent. CO_2.

In the above calculation the air has been taken as dry. If it had been saturated with water vapour the difference in percentage of so small a constituent would have been insignificant, namely 18/762 of the calculated amount, or 0·0017, making the result 0·066.

There is no sound objection to the method of water displacement for filling the bottles with air. A consideration of the solubility of carbon dioxide in water of which one volume

	At	0° C.	dissolves	1·713 volume
	„	10°	„	1·194 „
	„	15°	„	1·019 „
	„	20°	„	0·878 „
and	„	30°	„	0·66 „

shows that at ordinary temperature the concentration of carbon dioxide in liquid and gas phases is the same, so that any residual water left in the bottle, which will have become in equilibrium with the air to be tested during the course of pouring out the bulk of water, will contain just as much carbon dioxide as the same volume of air. Taking the extreme cases of 0° and 30°, we find that in emptying a two-litre bottle which has been filled with water about 4 c.c. remain. This will contain at 0° as much CO_2 as 6·85 c.c. of air, and at 30° as much as 2·64 c.c. of air, so that, using a bottle containing 2000 c.c., the error is:—

$$\left.\begin{array}{ll} \text{At } 0^\circ\text{C.} & \dfrac{6.85-4}{2000} = +.0014 \\ \text{At } 30^\circ & \dfrac{4-2.64}{2000} = -.00068 \end{array}\right\} \text{of true amount of } CO_2.$$

These errors are inappreciable but care must be taken to use distilled water, or at least water which is free from carbonates or bicarbonates, although even with ordinary tap water the error does not exceed about 0·5 c.c. CO_2 or, say, 2·5 c.c. in 10,000. This could

be allowed for, but it is of the same order as the CO_2 content of pure air. The weight of the bottles full of water is a point to be considered in connection with this method of sampling.

3. Aqueous Vapour.

The determination of aqueous vapour may be considered either as a physical or chemical process, according to taste. For determination with reasonable accuracy of the water vapour present at a given time in air, physical hygrometry is convenient, and for meteorological purposes these methods are always used. For many years Mason's wet and dry bulb hygrometer has been used to the exclusion of almost all others, but recently the dew-point instruments have been found to possess some advantages and have been used in various improved forms. Ezer Griffiths, who has given much attention to hygrometry, has devised various forms of Regnault's instrument in which the dew-point is observed on a slowly-cooled bright metallic surface. This method is also used in physical chemistry. Ezer Griffiths and J. H. Awbery have also described a hygrometer depending on the change of refractive index of glycerin due to the absorption of water. They consider their instrument to possess the following advantages and disadvantages: (1) Although it requires a definite setting to be made before the humidity can be obtained, the refractive index scale (an Abbe instrument is used) could be engraved directly in humidity so that the instrument is simpler than a wet and dry bulb hygrometer, or than the dew-point instrument, in that there are no calculations necessary. (2) Its lag is about fifteen minutes. In many cases this would not be excessive. (3) It is portable and reasonably robust. An old instrument which has been resuscitated is the hair hygrometer of de Saussure,[1] used very largely as a recording instrument. This has been investigated by F. J. W. Whipple, who says, "As a practical instrument for the measurement of humidity, the hair hygrometer has many advantages over its rival the psychrometer. Hair hygrometers are in general use in countries where temperature is below the freezing point for a large fraction of the year, in conditions in which it would be impossible to obtain satisfactory results with the ordinary psychrometer. Moreover, the hair hygrometer lends itself to adaptation as a recording instrument, and as such it is frequently seen in this country." He points out its merits for flights above the clouds into regions where temperature is below the freezing point.

The ordinary wet and dry bulb hygrometer is not a very satisfactory instrument owing to the irregular ventilation of the wet bulb. Whipple, who has also discussed this instrument, says that "it has long been realised that no system of hygrometry which depends on

[1] *Proc. Phys. Soc.*, 1922, **34** (ii.), 50.

the readings of a wet bulb thermometer with indeterminate ventilation can be satisfactory." In America whirling is used to secure full ventilation, but the most definite form of instrument is the Assmann pattern which is provided with a clockwork-driven fan. This arrangement ventilates both bulbs equally with the air of the *locus in quo* and enables precise determinations of humidity to be made.

A very ingenious instrument has been described by E. K. Rideal and A. Hannah[1] which depends upon the loss of volume of air when the aqueous vapour is removed by strong sulphuric acid; the definite volume of air used is remeasured at the same temperature and pressure as at first.

The above remarks will serve to indicate what instruments are available and their suitability for various purposes. When the chemist wishes to determine the absolute humidity over a period the simple method of passing a known volume of air through tubes containing strong sulphuric acid, which will increase in weight by the amount of water contained in the known volume of air, can be used. The drying system may serve as a preliminary to the gravimetric determination of carbon dioxide which is frequently required in investigations of the kind which he is called upon to undertake.

Humidity may be expressed either as the absolute amount of water in a given volume of air or as a percentage of the amount required for saturation. The following table will enable the necessary calculations to be made:—

Saturation Pressure of Aqueous Vapour (Scheel and Heuse)

(In mm. of mercury)

°C.	0	1	2	3	4	5	6	7	8	9
0	4·58 (4·84)	4·93 (5·18)	5·29 (5·54)	5·69 (5·92)	6·10 (6·33)	6·54 (6·76)	7·01 (7·22)	7·51 (7·70)	8·05 (8·21)	8·61 (8·76)
10	9·21 (9·33)	9·84 (9·93)	10·52 (10·57)	11·23 (11·25)	11·99 (11·96)	12·79 (12·71)	13·63 (13·50)	14·53 (14·34)	15·48 (15·22)	16·48 (16·14)
20	17·54 (17·12)	18·65 (18·14)	19·83 (19·22)	21·07 (20·35)	22·38 (21·54)	23·76 (22·80)	25·21 (24·11)	26·74 (25·49)	28·35 (26·93)	30·04 (28·45)
30	31·82 (30·04)	33·70 (31·70)	35·66 (33·45)	37·73 (35·27)	39·90 (37·18)	42·18 (39·18)	44·56 (41·3)	47·07 (43·5)	49·69 (45·8)	52·44 (48·2)

Figures in brackets = grams/cubic metre = mg./litre

4. Nitrogen

It is sometimes a matter of importance to determine whether the gas which has resisted the action of the various absorbents and of explosion, if that method of analysis has been used, is actually

[1] *Analyst*, 1915, 40, 48.

atmospheric nitrogen, and is therefore air-derived, or is pure nitrogen derived *e.g.* from the decomposition of organic matter. Treatment of the residue, first with heated copper oxide, which will oxidise methane or other hydrocarbons to carbon dioxide and water, and then with a suitable heated metallic mixture which will absorb nitrogen, forming metallic nitrides, if the reagents are pure, will leave a residue of argon and its congeners. Actually the residue is usually contaminated with acetylene or other hydrocarbons formed from

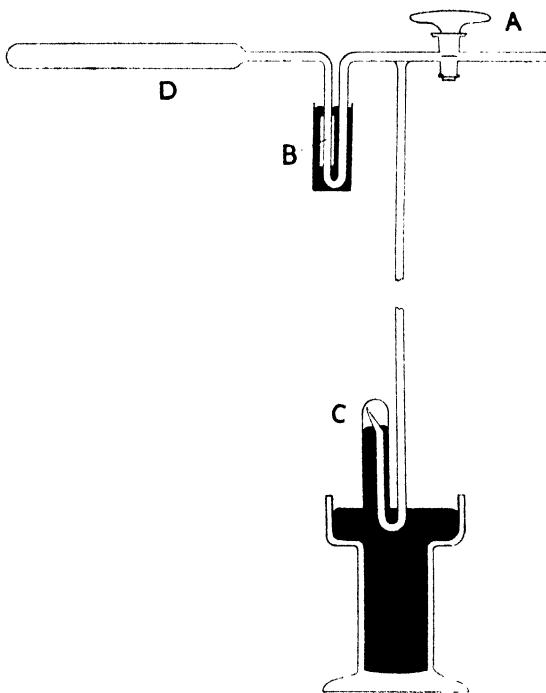



Fig. 92.

carbides in the metals. This can be removed either by sparking with oxygen or by combustion with copper oxide.

We have found the arrangement to be described very convenient for this purpose; but of course the process requires somewhat skilled manipulation and would only be used in cases where the origin of the nitrogen was a matter of importance. A good Antropoff or Sprengel pump is required and to the phosphoric oxide tube, which is usually fused on to the exhaust tube, a further attachment is joined, either by an all-glass joint or in the manner shown, which is due to Antropoff and is very convenient (Fig. 92). This attachment consists of a stopcock A, on the far side of which is fused a side tube B of capillary bore, about 1 metre long, upturned as shown and drawn out

at C to a fine point in a slanting and upward direction. As the point must be easily broken it is well to blow out the capillary a little so that the glass of the point is thin. The tube from the stopcock is upturned close to itself so that the temporary joint at B can be immersed in a jacket of mercury, so as to avoid leaks. At B a piece of rubber pressure tubing is fitted so that the tube D containing either copper oxide or the metallic absorbents may be attached. (An alternative construction with Antropoff joint is shown in Fig. 93.) A tall mercury trough or tower is needed in which the sealed bent part at C can be immersed until the point is covered.

When it is desired to absorb the nitrogen from a residual gas, and it is considered possible that combustible gases may be present, a hard glass or silica tube is prepared containing copper oxide and drawn out as shown at D. This is heated by suitable means, *e.g.* an electric tube-furnace or a small gas-heated tube-furnace. The tap A is opened and the whole system exhausted while the oxide is being heated, care being taken not to let it get hot enough for the walls to fall in, which may easily happen. When the air is all pumped out of the apparatus, A is turned off and the gas, in a small tube, brought over the mercury tower, which is placed under the inverted syphon at C and then raised until the point is well covered by the mercury. The tube containing the gas is then brought over the end of C so that when the mercury trough is lowered the sealed point may be within the gas space. By carefully breaking the point against the side of the gas tube, which must be fairly strong, and manipulating the gas tube the whole of the gas except for the small portion retained in the upper part of the long tube will pass into the heated tube D. Diffusion will ensure that the whole of the gas is subjected to the action of the heated copper oxide. After, say, fifteen minutes' contact the tap A may be turned to connect the gas in D with the pump, and the latter is worked so that D is completely evacuated, the gas being collected in a suitable small tube for remeasurement and, if necessary, absorption of carbon dioxide. This treatment is necessary only when the presence of combustible gases is suspected. The actual absorption of nitrogen is carried out in a similar tube to D, but about half filled with a mixture of one part of magnesium and five of freshly ignited quicklime. This mixture may be made up in amounts sufficient for a few determinations, but it is important to keep it perfectly dry, as otherwise there is risk of explosion when it is heated. We have found that with

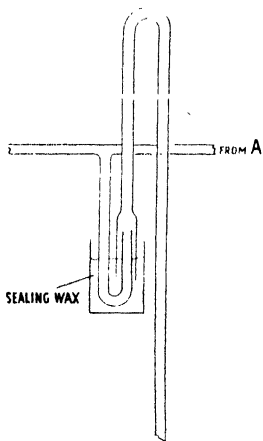



Fig. 93.

ordinary magnesium powder a rather long period of preliminary heating is necessary, as the mixture gives off gas which the smell of the used mixture left in the tube when the apparatus is disconnected suggests is acetylene. Before connecting it is necessary to blow out the mercury from the long capillary, and to reseal the end C. The tube is connected in the same way as the copper oxide one, exhausted, then heated to a dull red and the pump worked so long as gas is given off. The gas evolution having ceased, the tube of residual gas from the previous operation is brought over the sealed end of C as before, the cock A turned off, and the end C broken again so that the gas enters D. A rapid rise of temperature occurs in the magnesium-lime tube and the mercury rises in the capillary owing to absorption of nitrogen. When the volume appears to have become constant the pump is started again and the gas all pumped out. The operation is repeated with copper oxide to burn any combustible gas and the residual gas treated with a drop of potassium hydroxide solution before measurement. The residual gas is argon with its congeners. The normal proportion of nitrogen to argon, etc., is 1 : 0·0121, or the total residual gas contains 1·20 per cent. of inert gas.

Alternatively a little copper oxide may be placed in the front of the magnesium-lime mixture, or the residual gas after absorption of nitrogen may be sparked with oxygen, the excess of this gas being absorbed with pyrogallate.

5. Carbon Monoxide

This gas is not a normal constituent of air, but there are some small indications that it may in time become one. The enormous increase of motor traffic in all countries, more especially in cities, seems to raise the presumption that carbon monoxide may accumulate in appreciable amounts in the air. It is true that the complete combustion of motor spirit yields only carbon dioxide and water, but analyses of exhaust gases shows that complete combustion is unusual, and that a very large proportion of the carbon of such fuel escapes as carbon monoxide. Recent work on this point by Cambier and Marcy[1] has shown that a small but appreciable amount—from 1 to 5 parts in 100,000 — is to be found in the air of Paris at the height of the nose and mouth, and up to 13 parts at the height of a motor exhaust in congested traffic. It should be said that the higher results at 1·6 m. above ground were found during traffic blocks in one-way streets and represent transient conditions. Having regard to the relative width of the streets of Paris and those of most English cities, it is likely that the Paris figures are fair samples of city con-

[1] *Comptes rend.*, 1928, **186**, 918 ; see also E. Kohn-Abrest, *Chem. and Ind.*, 1928, **20**, 30 ; and Florentin, *Comptes rend.*, 1927, **185**, 1538.

ditions. It is known that in roads through tunnels the proportions may become dangerously high. Garages and all enclosed places where internal combustion engines are allowed to run are almost certain to be dangerous at times unless very great precautions are taken. The United States Public Health Service[1] has recently examined the air of fourteen large cities in that country. "The average of 141 tests made in city streets at peak hours of traffic showed a contamination of 0·8 parts of carbon monoxide per 10,000 parts of air. Only 24 per cent. of all the street samples had more than 1 part of carbon monoxide in 10,000 of air, and in only one location, a covered passage-way, was there as much as 2 parts per 10,000. Samples taken inside autobuses yielded even lower concentrations of carbon monoxide gas. The figures for street air, when viewed in the light of present-day standards of exposure to carbon monoxide, do not reveal the existence of a health hazard from this source in our city streets." The standards referred to are those proposed by Dr Henderson, who did a great deal of work on this subject for the New York and New Jersey State Bridge and Tunnel Commission.[2] He formulated the following general rule: When the time is measured in hours and the concentration of carbon monoxide in parts per 10,000 parts of air, the physiological effects may be defined by the equations :—

Time × concentration = 3, no perceptible effect.
Time × concentration = 6, a just perceptible effect.
Time × concentration = 9, headache and nausea.
Time × concentration = 15, dangerous.

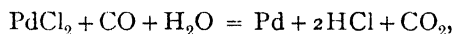
This work was confirmed by Sayers, Meriwether and Yant,[3] who studied the effect of long exposure to low concentrations of carbon monoxide, the effect of strenuous exercise and the effect of high temperature and humidity on low concentrations. They showed that when a subject exercised strenuously for one hour in an atmosphere containing 2·5 parts of carbon monoxide in 10,000, the immediate symptoms of carbon monoxide poisoning were moderate and the after-effects mild to moderate. None of the subjects showed any permanent effects after repeated exposures to carbon monoxide.

There is an air of optimism about all this work which seems a little out of accord with our general notions of this very deadly gas. We feel that in any specific case coming under the analyst's notice where he is called upon to advise as to standards, it would be wise to regard the standards proposed by the American workers as the utmost limits which should under any circumstances be allowed. It must be kept in mind that natural ventilation is relied on for the

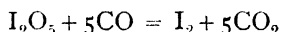
[1] *Rep. U.S. Public Health Service*, 1928, Reprint 1217.
[2] *J. Ind. Hygiene*, 3, Nos. 3 and 4, pp. 79, 137.
[3] *U.S. Public Health Report*, 1922, 37, No. 19, Reprint 748.

removal of carbon monoxide from streets. It is known that such ventilation almost completely fails occasionally, as considered by the dense collection of smoke in the streets, usually referred to as a "smoke fog." It is during such periods that danger may exist, as traffic blocks are usual accompaniments of such condition and it does not appear wise to dismiss the possibility of danger to health.

Determination of Carbon Monoxide.—The ordinary methods of gas analysis (absorption by cuprous chloride, either acid or ammoniacal, or combustion over copper oxide heated to about 400°) are not sufficiently delicate for its determination either in ordinary air or in the exhaust gases of the more efficient fuel-burning appliances, as the amounts are of the order of 0·00001 to 0·1 per cent. Two other methods are available—absorption by defibrinated blood, which is specific, and the much more delicate reaction with iodine pentoxide, which is not, but can be made so by the careful removal of other gases which would liberate iodine from this compound. Other reactions have been proposed and used for this purpose. Among these is one with palladium chloride which is reduced to metallic palladium according to the reaction—

$$PdCl_2 + CO + H_2O = Pd + 2HCl + CO_2,$$

and has some advantages for qualitative detection.

Iodine Pentoxide Method. The most trustworthy method of determining the very small quantities of this gas which are likely to be found in air is by oxidation to carbon dioxide by iodine pentoxide. The reaction

$$I_2O_5 + 5CO = I_2 + 5CO_2$$

proceeds quantitatively under well-defined conditions, and either of the products may be determined as a measure of the monoxide originally present. Nicloux and Gautier independently suggested the use of the reaction, Nicloux determining the iodine liberated whilst Gautier determined the carbon dioxide. Of the two methods, the iodometric is the more sensitive and more commonly used. The process is not specific, that is, iodine pentoxide will oxidise other substances which may be present in air, such as unsaturated hydrocarbons. It is, therefore, necessary to remove these and all other interfering substances by appropriate absorbents. We have found the arrangement and method of working described below to be convenient and to yield very low "blanks"; one of the difficulties of the process as sometimes carried out is the persistent appearance of traces of iodine coming over from the pentoxide when air known to be free from carbon monoxide is passed over it. It is necessary to allow purified air to pass over the heated pentoxide for about a month in order to reduce the blank to 5 parts per million. This

ESTIMATION OF CARBON MONOXIDE BY MEANS OF IODINE PENTOXIDE

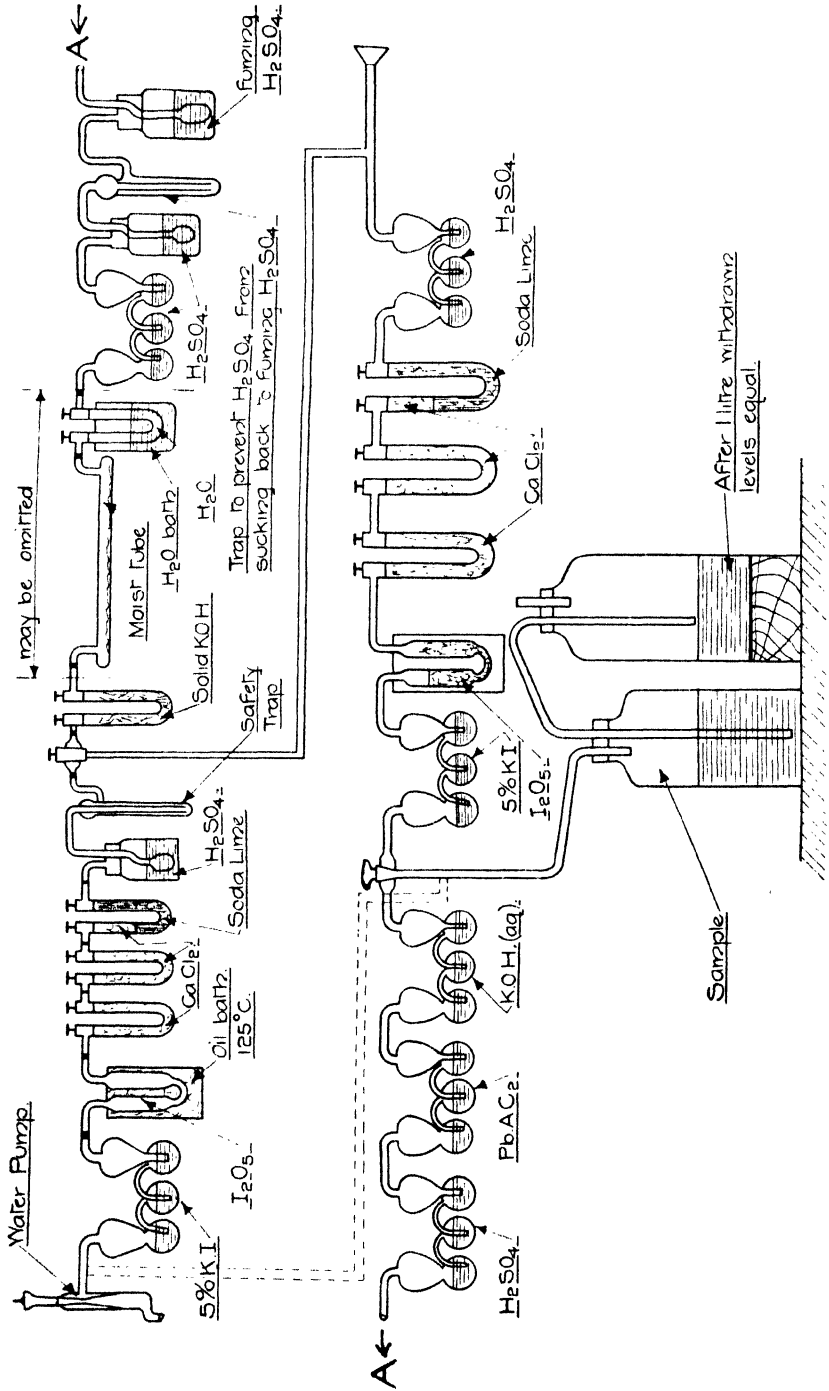



FIG. 94.

involves no trouble; it only requires that the apparatus must remain permanently set up (which means that it is always ready for use), and that a continuous stream of air must pass through it; a water pump and a small burner must be kept going. That is all the care needed to obtain so desirably small a blank.

In the form of apparatus we have used (Fig. 94), the air to be examined passes through three Geissler potash bulbs containing respectively strong aqueous potash, lead acetate solution and strong sulphuric acid. The dry gas freed from acid gases, especially hydrogen sulphide, then passes through fuming sulphuric acid to remove unsaturated hydrocarbons, through a safety tube to prevent backflow of acid from the next tube and Geissler bulbs which both contain strong sulphuric acid to absorb sulphur trioxide which may be carried

LIQUID AIR APPARATUS (FOR CO DETERMINATIONS)

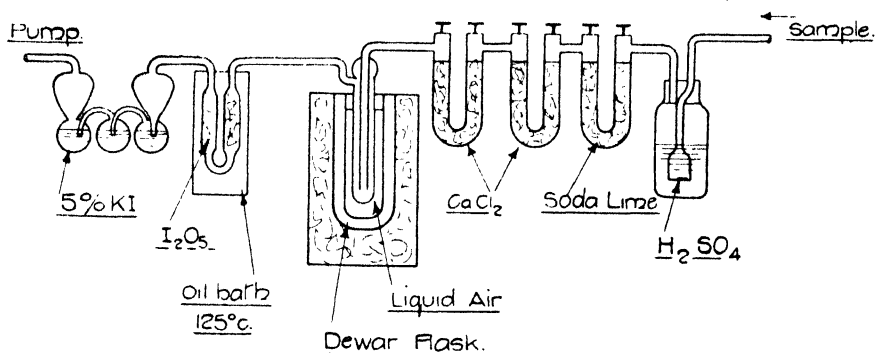



FIG. 95.

over, a U-tube with a little warm water and a long horizontal wetted tube serve effectively to hydrate any SO_3 which may have escaped the sulphuric acid. A U-tube filled with solid potash is followed by a three-way tap the use of which will be explained later. Another safety tube is followed by a U-tube with soda lime and two calcium chloride tubes. The air, freed from all impurities but vapours of saturated hydrocarbons, may now if desired pass over the iodine pentoxide; but it is better, if it can be done, to let it first flow through a condenser tube immersed in a Dewar tube with liquid air (Fig. 95). The pentoxide, either in a U-tube as shown or in a long straight tube, is uniformly heated to a fairly constant temperature of 120° to 130°. The liberated iodine is absorbed in a 5 per cent. solution of potassium iodide. It is convenient to work on a 1 litre sample of air. A Winchester quart bottle filled with water can easily be emptied by inversion in the air to be tested, and the previously greased stopper replaced, the bottle labelled and sent to the laboratory. Here it can be opened under water, a suitable fitting put in the neck and the

determination made. The air may pass through the apparatus at the rate of about 4 litres an hour. The final titration of iodine is made with $N/500$ thiosulphate, using as indicator a solution of soluble starch containing 0·5 g. per litre.

When all the measured volume of air has passed into the apparatus, this is swept out by air which has passed through a similar purifying train to that used for the sample, including the pentoxide tube. In our arrangement this train is connected by a three-way tap to the exit from the sample bottle. A determination can be made in about two and a half hours. It is advisable, if a determination may have to be made at any time, to keep air always passing over the heated pentoxide, so that it may not yield free iodine when first heated. As to the use of liquid air, we have found that air from a roadway tunnel much used by motor traffic yielded one-third more iodine when liquid air was not used than when it was. It is therefore desirable to multiply results by 0·75 to obtain a correct figure when absorbents only are used.[1]

6. Oxides of Nitrogen

A very small proportion of oxides of nitrogen, mostly, it may be presumed, nitrous anhydride, appears to be normally present in air. A study of methods for their determination has been made by A. G. Francis and A. T. Parsons,[2] who have described two methods of applying a modification of the process of oxidation by hydrogen peroxide used by Allison, Parker and Jones. The original process of the latter authors was to oxidise with an alkaline solution of hydrogen peroxide and to determine the nitrate formed by conversion into the nitro-compound of phenol-disulphonic acid after the method of Grandval, used in water analysis (*cf.* p. 405).

Francis and Parsons found that this process was inadequate, as nitrite was always found when the solution was tested with the Griess-Ilosvay solution. Oxidation in neutral solution gave better results, whilst in acid solution nitrous acid was oxidised by hydrogen peroxide completely. They evolved the following method of determining nitric oxide present in proportion over one part in a million. The solutions required are as follows:—(1) Hydrogen peroxide, 50 c.c. of 7·5 per cent. hydrogen peroxide (25 volumes) and 1 c.c. $2N$ sulphuric acid were diluted to 100 c.c. 7 c.c. of this solution were used for each experiment. The hydrogen peroxide should contain no organic preservatives and not more than minute traces of nitric acid, from which no specimens examined were entirely free. The best sample showed a blank equal to 1·0 c.c. of

[1] Sometimes a considerable volume of liquid condenses in the tube immersed in liquid air, through which the air to be examined is passed. This is mainly oxygen condensed by the new liquid air, and when liquid air remaining over on the second day is used, no appreciable condensation takes place.

[2] *Analyst*, 1925, 50, 262.

standard nitrate solution (1 c.c. = 0·001 mg. N) in the quantity required for each experiment. (2) Normal potassium hydroxide. Most samples (also of sodium hydroxide) contain traces of nitrite. Specimens free from this impurity must be chosen. (3) Phenol disulphonic acid. This reagent is prepared according to the method of the American Public Health Association, as follows:—Dissolve 25 g. of pure white phenol in 150 c.c. of pure fuming sulphuric acid (15 per cent. SO_3), stir well and heat for two hours at about 100°. (4) Standard potassium nitrate solution (1 c.c. = 0·001 mg. N). Dissolve 0·72 g. of pure recrystallised potassium nitrate in 1 litre of distilled water. Evaporate 10 c.c. of the solution cautiously to dryness on the water-bath. Moisten the residue quickly and thoroughly with 2 c.c. of phenol disulphonic acid and dilute to 1 litre. This is the standard solution, 1 c.c. of which equals 0·001 mg. of nitrate nitrogen.

Tests were carried out as follows:—A water pump was used to aspirate the products of combustion for some time through a clean, dry, empty bottle of known capacity (about 1 litre). Clearly any other means of aspiration through a dry bottle could be used. The bottle was fitted with inlet and outlet tubes passing through a well-fitting 2-holed rubber stopper that had previously been boiled with caustic alkali and well washed with water. The outlet tube was in the form of a tap funnel. After the sample bottle had been disconnected from the current of gases, 7 c.c. of the hydrogen peroxide mixture was added to it through the tap funnel. The end of the inlet tube was then sealed with a cap of pressure tubing and glass rod, and the bottle rotated so that the inner surface of the bottle was thoroughly wetted by the liquid. The bottle was set aside and rotated frequently during three hours; after this, absorption of the oxides of nitrogen was complete. The preliminary experiments showed that sufficient time would thus be allowed for absorption and oxidation. The solution was then rinsed into a flat porcelain dish of 50 c.c. capacity, where it was made just alkaline to litmus by 0·5 to 1·0 c.c. of $N/1$ KOH, and evaporated to dryness on an electrically heated water-bath (to avoid the possibility of absorption of oxides of nitrogen formed during combustion of gas). When dry the residue in the dish was allowed to cool, and was then moistened with 2 c.c. of the phenol disulphonic acid reagent. The acid liquid was now diluted, made ammoniacal with 15 c.c. of ammonia solution (1 vol. NH_4OH solution, sp. gr. 0·880, to 1 vol. water) and brought up to 100 c.c. This solution was then compared with the standard solution in Nessler tubes.

It was rarely necessary to filter the solution, as the quantity of alkali used is very small and the consequent action on the vessels negligible. Blank tests, run side by side with the experiments, showed quantities of nitrate varying from 1·0 to 1·5 c.c. of standard solution

equivalent to 1·0 to 1·5 thousandths of a milligramme of nitrogen and the appropriate deduction was invariably made. The results given in the paper are satisfactory, the errors reaching ± 6 per cent. when the proportion of nitrogen added as nitric oxide was from 20 to 30 per million of air.

The authors of the above process mention that in the investigation in which it was used the determination of carbon monoxide was also carried out by the iodine pentoxide method, liquid air being used to remove condensable gases. A blue solid, presumably N_2O_3, was frequently observed in the condensing tube, and this solid had a nitrous odour and reacted with potassium iodide and with the Griess-Ilosvay solutions. It was therefore thought that the condensed products could be employed for determining the oxides of nitrogen either as an alternative to the method described above, or for obtaining quantitative values when they were in extreme dilution. A method for doing this was therefore devised and is described in the paper.

Some results obtained by Francis and Parsons at St James' Square, S.W., are given below:—

1923.	Oxides of nitrogen as NO_2. Parts per 100 million by volume.	Remarks.
July 2	3·7	Motors about.
Sept. 4	0·8	Dull wet day after heavy rain.
,, 5	1·0	Bright sunny morning.
,, 10, 10 A.M.	2·0	No rain since Sept. 4. Fine dry day.
,, 10, 2 P.M.	1·8	......
,, 11	1·9	Fine dry day.
,, 13	1·1	Fine dry day but windy.
,, 14	1·1	Fine sunny day. No rain.
,, 15	5·8	Fine day. Motors about.
,, 18, 11 A.M.	0·3	Showery morning after much rain.
,, 18, 2 P.M.	0·3	......
,, 19	1·0	Fine day. Motors about.
Nov. 26, 11 A.M.	16·8	Cold foggy day.
,, 29, 2 P.M.	2·5	Dry dull day after rain in the night.
,, 30, 2 P.M.	2·2	Cold bright day.
,, 30, 6 P.M.	10·7	Fog came up about 4 P.M.

The amounts are very small. Nitrous acid appears to be associated with fog and to be removed by heavy rain.

The method, which appears to be the best available, has the great advantage of being specific, as it depends upon the formation of a nitro-compound and not upon an indirect action, such as the liberation of iodine, which is more a measure of oxidising substances.

7. Hydrogen Sulphide

This is one of the most poisonous of gases, although it is difficult for anyone who has worked in a chemical laboratory used by students for qualitative analysis to realise this. The very strong smell of the

gas must be the reason why its toxicity is so little recognised, since, according to Lehmann, most persons can only tolerate about 0·01 per cent. in air, while three persons examined by him suffered very painful irritation of eyes, nose and throat when breathing an atmosphere containing 0·02 per cent. for from five to eight minutes. A very dangerous feature of this gas is the fact that as the concentration increases the smell seems to become less marked or rather to alter in character, losing the characteristic odour of rotten eggs and becoming sweetish. There is no recovery from the collapse which follows breathing air containing a few per cent. of this gas. It may be useful to note that a fatal case occurred some years ago at the Cape of Good Hope Observatory consequent on the use of a mixture of iron turnings, sal ammoniac and sulphur for making rust joints, the sulphur having been added, as is sometimes done, to accelerate the action. This apparently it did, causing heating and a copious evolution of hydrogen sulphide. It is clear that in confined spaces iron and sal ammoniac only should be used.

Detection. The usual means of detection of this gas is by lead acetate papers which, especially if moist, are very readily stained brown or black by very small traces. The papers may be hung up in the atmosphere to be tested, or the air may be passed over or through a fragment of lead paper probed into a narrow glass tube.

One of us has used a syringe in which a small piece of test paper is arranged in a small nozzle with an aperture through which the air is drawn by working the piston in the usual manner. A small circular stain is produced by the merest trace of the gas.

Determination of Hydrogen Sulphide.—It would be fairly easy to develop a quantitative process from the lead acetate paper test by preparing a standard set of stains, or better, a matched set of tints with a permanent brown or brown and black water-colour wash and, either by the syringe method mentioned above or by using an ordinary aspirator, passing a known volume of air through the paper so that the whole of the sulphuretted hydrogen is absorbed by the lead in the paper.

A very elegant process, based on the formation of methylene blue by the Caro-Emil Fischer[1] reaction has been worked out by Autenreith and Breh. When *p*-aminodimethylaniline and a sulphide in acid solution are treated with ferric chloride a blue colour develops in the course of half an hour even when the amount of sulphur as sulphide amounts to less than a thousandth of a milligramme.

The air to be tested is drawn through a series of wash-bottles or other suitable scrubbing devices, containing sodium or potassium hydroxide. The quantity needed for a determination will vary

[1] *Ber.*, 1883, **16**, 2234.

according to the amount of hydrogen sulphide it contains, but from the description given about 20 litres is a suitable amount. This is drawn through the absorbing train at the rate of about 20 litres an hour. A gas meter or other measuring device is used and, when all the gas is passed, the alkali in each vessel is rather more than neutralised; it is clearly advisable to know the strength and amount of alkali used so that an appropriate amount of acid can be added without question. To the contents of all but the last absorbing vessel mixed together a few mg. of *p*-aminodimethylaniline hydrochloride is added and then a few drops of ferric chloride solution. After about half an hour a blue colour will have developed if hydrogen sulphide was present in the air. In this case a similar test should be made on the acidified contents of the last vessel of the absorbing train, which should not yield a blue colour, as this would show that air had been passed at too rapid a rate, and the absorption might be incomplete. Assuming that the experiment was satisfactory, the colour of the solutions must be matched with solutions of methylene blue which have been standardised against colours produced by known amounts of sulphide. This can be done by preparing a very dilute solution of the gas and titrating it with iodine ($N/100$) and then developing the methylene blue colour in a portion, subsequently using this for preparation of the standard tints. Autenreith uses a colorimeter in which a hollow glass wedge capable of movement so as to expose varying thicknesses contains the standard liquid, the comparison being made by means of a prism device which brings the two fields into close juxtaposition; but of course any other comparator can be used. The order of accuracy does not appear to be high but the difficulty of determining a constituent present in very small quantity is naturally very great, and the order of content is more important than the actual figure. The full description has not been published, but sufficient details to enable an intelligent worker to use it are given in Autenreith's well-known work on poisons.[1]

8. Sulphur Dioxide and Sulphuric Acid

The determination of oxides of sulphur in air has recently assumed great importance in view of the erection of "super" power-stations in various parts of the country. Unfortunately the methods available have not been well investigated and are more or less in the experimental stage. One for sulphur dioxide, which was used as long ago as 1891 by Dr T. Lewis Bailey, appears to be sound and, in a modified form, is being investigated by the Atmospheric Pollution Committee of the Department of Scientific and Industrial Research, to whom it has been recommended by the Government chemist who has developed a

[1] W. Autenreith, *Detection of Poisons*, 6th edition, 1928, p. 658.

technique. It consists in bubbling the air to be examined through a solution of hydrogen peroxide which oxidises sulphur dioxide to sulphuric acid. This may be determined if the absorbing liquid has first been neutralised by titration with *N*/25 alkali, or the liquid may be concentrated to small volume and the sulphate determined as barium sulphate. For the latter a very good balance would be needed, as the amounts likely to be found are of the order of 1 mg. of SO_2 per cubic metre (= 35·31 cubic feet). Bailey's work is very interesting, as it deals with the effect of sulphurous gases on vegetation and with many interesting aspects of this form of pollution.[1]

An ingenious micro-method has been suggested by A. C. Röttinger, but it is difficult to see how he obtains any result from air which is not

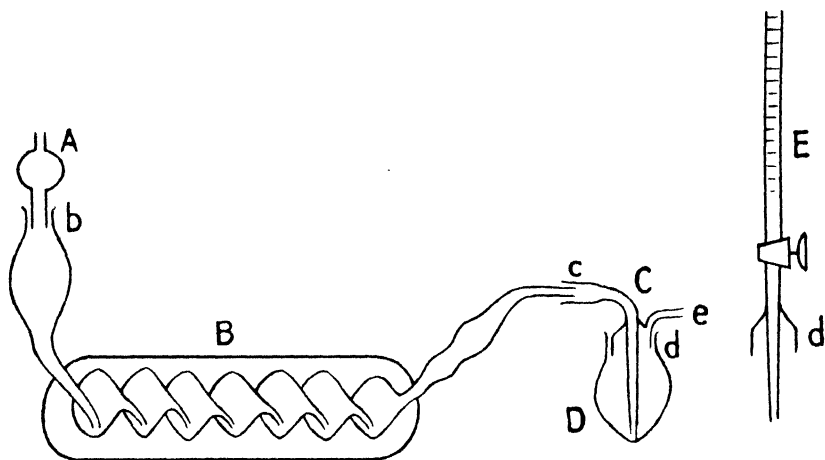



FIG. 96.

absolutely choking when working with 1 to 2 litres. It should, however, be useful with larger volumes and for flue gases, and is given for those who may care to experiment with it.

Röttinger's method[2] is as follows:—"In the assessment of agricultural damage by fumes, the determination of sulphurous acid in the air plays an important part. The determination as usually made hitherto is very elaborate, since one must suck 20 litres or more through an absorption apparatus which, naturally, in the field is not only very tedious, but also is subject to many sources of error.

"A micro-apparatus (see Fig. 96) is described which has been well tested and which permits a determination to be made with only 1 to 2 litres of air, drawn through the apparatus by an appropriate aspirator.

"At A a plug of cotton-wool is provided for the filtration of the

[1] *Proc. Manch. Field Naturalists' and Archæolog. Soc.*, 1889 and 1892.

[2] *Microchem.*, 1929, *Pregl.-Fest.*, 313.

entering air, which by suction at *e* is made to pass through the absorption vessel B, into which 10 c.c. of 0·01*N* iodine solution is introduced, and by gentle aspiration at C this is distributed through the first few bulbs. By further passage through it of the air stream the liquid passes into the further bulbs. At *c* the delivery tube C is arranged in the little flask D which contains 10 c.c. 0·01*N* thiosulphate solution, which intercepts any iodine carried over. When the air has all passed through the system, the contents of B are washed into D, C being removed and washed out. For this washing out distilled water is to be used that has been previously allowed to stand for several hours with 5 c.c. of 0·1*N* iodine solution, and then after the addition of starch solution exactly decolorised by 0·1*N* and finally 0·01*N* thiosulphate solution. The micro-burette E, which holds 5 c.c. and is divided into 0·02 c.c., is passed through the opening *d* so that its jet reaches to the bottom of D. This jet is so fine that with a moderately rapid opening of the tap only a fraction of a division flows out. By means of this burette the contents of D are titrated after the addition of starch solution."

The chief advantage of the absorption vessel B lies in the fact that it combines good absorption with ease of washing.

The detection of sulphuric acid—it would not remain long as sulphur trioxide—in air is very difficult, as it is present not as a gas, but as a suspension of droplets. The difficulty of absorbing such suspensions is fairly well known. Whereas the violent movements of the molecules of a very soluble gas usually ensure complete absorption by bubbling through an appropriate liquid absorbent, those of particles or droplets, which are Brownian, are relatively slow and of small amplitude, so that penetration of the interface seldom occurs.

9. Ozone

The presence of ozone in air has been the subject of much discussion. The tests which were formerly considered to prove its presence are not specific to ozone but would give indications with hydrogen peroxide and nitrous acid, both probable constituents of air. Ch. Fabry, from an examination of the absorption of ultra-violet in the solar spectrum, concludes that the ozone content of the whole thickness of the atmosphere is equal to a layer of pure gas 3 mm. in depth. He says[1]: " If the layer of 3 mm. were uniformly distributed, the proportion of ozone would be 4×10^{-7} by volume, or 60 mg. per 100 kg. of air, by weight. The chemical estimation of very small quantities of ozone appears to be a very uncertain operation. The most reliable measurements give proportions of this gas very much lower than the figures I have just mentioned. Lespieau finds at the surface of the earth

[1] *Proc. Phys. Soc.*, 1926, **39**, 11, 12.

3 mg. of ozone per 100 kg. of air; he finds the same proportion at the top of Mont Blanc, at a height of 4800 metres." Fabry concludes that, "It is certain then, that the quantity of ozone disclosed by the study of the solar spectrum is not furnished by the lower atmosphere, or even by that part of the atmosphere which is accessible on a mountain." This conclusion is shared by Dobson and Harrison, who say[1]: "It has been shown that there is no appreciable quantity of ozone near the surface, and all that there is, is probably above the troposphere."

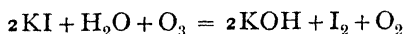
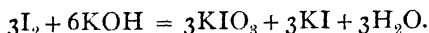
The presence of ozone is therefore unlikely in natural air, but its determination is of interest when it is used in conditioning air, as in some tube railways. Fabry's remarks about the chemical estimation of ozone are fully justified, but the following method is given for what it is worth.

Determination of Ozone.—The methods which have been proposed for determination of ozone in air are for the most part based on the oxidising power of this gas and are mostly non-specific; that is, any other oxidising gas, such as oxides of nitrogen or hydrogen peroxide would, if present, be considered as ozone. The following reactions, among others, have been suggested as suitable :—

(1) The liberation of iodine when ozone acts on potassium iodide in solution and the subsequent reaction of the iodine with starch. This test was long ago recognised as non-specific and the detection of the alkali also liberated, by means of litmus, suggested. As iodine is not without action on litmus this reaction also is useless, although it is not given by acid gases which form salts with the potassium ion. Other reactions involving the iodide reaction have been proposed. Hatcher and Arny based a method on the slow formation of iodate from the iodine and potash

$$2KI + H_2O + O_3 = 2KOH + I_2 + O_2$$

and

$$3I_2 + 6KOH = 3KIO_3 + 3KI + 3H_2O.$$

The iodate is detected by means of the free iodine liberated on acidifying, and is determined by titration with thiosulphate. These workers also used the oxidising action of ozone on a solution of potassium arsenite, which is oxidised to arsenate. The loss of arsenite was determined. These two methods gave very different results and the problem does not seem to have been resolutely faced. Hayhurst and Pring used a solution of potassium iodide protected from the light, and examined the solution afterwards for free iodine, free alkali, and potassium iodate. "In this way," they say, "an estimation could be made of the ozone (together with hydrogen peroxide) and of the oxides of nitrogen." Hayhurst and Pring showed

[1] *Proc. Phys. Soc.*, 1925, **38**, 74.

that their iodate process was satisfactory when there was any ozone to determine, which they, like most other careful workers, found was not the case either at the ground level at Glossop Moor or, in kite experiments, up to a level of 8000 feet. The method would, apparently, be satisfactory when it was desired to determine ozone in ozonised air, which is the only case of real interest. The apparatus used was of a special form in order to fit it for use with kites, but the iodide solution, which should be strong, can suitably be placed in any effective absorption apparatus and the very large volume of air needed aspirated by any available means.

(2) F. L. Usher and B. S. Rao, in 1917,[1] reviewed previous work, including that of Hayhurst and Pring, and concluded that the reaction with iodide was untrustworthy. They decided to use the reaction with nitrite in neutral or acid solution:

$$O_3 + NaNO_2 = O_2 + NaNO_3.$$

It appears from their work that, although hydrogen peroxide will oxidise nitrous acid to nitric, it has no action if the solution is slightly alkaline. Their technique, which is more definite than that of Hayhurst and Pring, is as follows:—

Two samples of air are taken in bottles each holding about 7 litres. One sample is passed through tubes containing chromic acid and manganese dioxide respectively. The other is passed only through a chromic acid tube. The first bottle will have been freed of both ozone and hydrogen peroxide and the second will contain ozone and nitrous acid if either or both of these should be present. The bottles are filled with very good distilled water after having been very carefully cleaned, and the air introduced by fitting into the neck a double bored rubber stopper fitted with one capillary tube reaching to the bottom of the bottle, and another reaching only through the cork but prolonged outside to about 30 cm. and with a tap sealed to the end. To the outer end of the capillary the absorption tubes are sealed. The bottles are filled by inverting them after fitting the stoppers and tubes and then opening the stopcocks so that air flows in at the rate of about 1 litre a minute. By filling in this way the air does not bubble through the water but only collects over it. The stoppers are replaced and, when convenient, the standard nitrite solution is added. This is a $N/40{,}000$ solution made with $N/1000$ sodium hydroxide instead of water. As this corresponds only to 1·725 mg. per litre, it is better to make up a stronger solution, say $N/1000$, and to dilute this. The amount recommended is 25 c.c. rapidly added from a pipette and followed by 100 c.c. of water. The bottle and its contents is then shaken on a machine for about half an

[1] *J. Chem. Soc.*, 1917, 111, 799.

hour and then the liquid is made up to 250 c.c., 50 c.c. is withdrawn into a 100 c.c. stoppered flask, 5 c.c. of Griess-Isolvay reagent added and the flask warmed to 75° for ten minutes. The colour of the pink azo-compound formed is then compared, in a Duboscq colorimeter, with that given by 5 c.c. of the standard nitrite diluted to 50 c.c. The loss of colour is clearly a measure of the amount of nitrite which has been oxidised to nitrate. The following formulæ are given by the authors for use in calculation:—

Let v = c.c. of air collected through chromic acid,
r = ratio of length of column of standard solution to that of column of experimental solution,

then the volume concentration of nitrogen peroxide will be 1 in $v/0{\cdot}014\,(r-1)$ of air. And if

v^1 = c.c. of air collected through chromic acid and manganese dioxide,
r^1 = ratio of length of column of standard solution to that of column of experimental solution.

the volume concentration of ozone will be 1 in $1/0{\cdot}007\,(r/v - r^1/v^1)$ of air, assuming that nitrite solutions of the strengths given above are used.

10. Vapours of Organic Substances, etc.

The air of works where volatile organic substances are used may be more or less saturated with the vapours of these substances, and the determination of such vapours may for reasons of economy or health be desired. A general method for separating such vapours from air is by passing it through vessels cooled in liquid air and merely condensing or freezing out the desired substances which can be afterwards examined. There are very few substances which have an appreciable vapour tension at the low temperature obtained by the use of liquid air, and the method has the advantage that no foreign substances are introduced. The details of working will, naturally, vary according to the needs of the case and the taste of the observer.

It is necessary, in the first place, to consider how the sample should be collected. When it is possible the best plan is, no doubt, to aspirate air, on the spot, through the condenser which is immersed in liquid air, and so avoid all chance of adsorption by the walls of the collecting vessel, by rubber stoppers or by grease used to make glass joints tight or by water used as a displacing or displaced fluid.

When very large volumes of air have to be measured, ordinary gas meters are more convenient than holders or aspirators. Small dry meters which will record up to thousands of cubic feet with an accuracy of 2 or 3 per cent., which is quite good enough, can be bought for a few pounds and are made by thousands, so that there is no difficulty about delivery. They are relatively light and portable, much more so than expensive wet meters. One thing must be remembered: the meter must follow, not precede, the absorbing train

or some selective absorption may occur in the dressed leather bellows. Meters should be officially tested and certified before sale. This is a very inexpensive matter.

For drawing the gas continuously through the absorbing system and meter, motor-driven blowers which can be used as exhausts can be obtained from most apparatus dealers, or water pumps can be used. It is necessary in buying a motor pump to make sure that it is designed to work at the voltage and frequency available. Direct current motors are best if they can be used, as variable speed is often an advantage. If a fixed speed motor must be used, it should be one which will drive the exhaust at the maximum rate which may be needed, and a less rapid passage of air through the absorbing train arranged by by-passing—that is by allowing only a part of the air passing through the pump to go through the absorbing system and meter.

Liquid air will condense not only vapours of organic liquids but water and carbon dioxide. Since absorbents of these substances are likely to absorb other compounds also (*e.g.* calcium chloride will take up alcohol, sulphuric acid absorbs alcohol, all bases, and many other substances, while potash or soda-lime will absorb any acid vapours), it may be advisable, unless the nature of the vapours is well known, to condense everything other than oxygen and nitrogen in the vessel cooled by liquid air and to separate the condensate into its constituents by subsequent treatment. The best method would be to condense in a small vessel which could be sealed off from the inlet system and also from the outlet and fitted with a capillary into which the vapour could be distilled. This could be done by removing the condenser vessel from the liquid air into, say, ice and dipping the capillary into the liquid air. By this means a separation of substances having a vapour tension much higher than that of water at 0° (4·6 mm.) will be effected. Considerable skill would be required to make the subsequent examination, but with care the difficulties should not be insuperable. It seems futile to suggest any specific methods, which can best be worked out for each case by studying the properties of the substances in a good book on systematic organic chemistry.

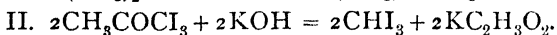
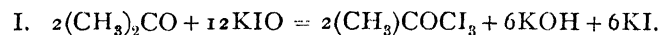
Some compounds can be separated more or less satisfactorily by means of absorbents. The principal difficulty is that there are hardly any absorbents which are really selective. Sulphuric acid, for example, will absorb all unsaturated, basic, or hydroxylic substances; a mixture of sulphuric and nitric acids will take up all aromatic hydrocarbons and most of their derivatives, with a host of other things. Carefully directed qualitative analysis on the microchemical scale will afford information as to the substances absorbed.

Special processes for some vapours are given below.

Elliott and Dalton[1] used the following combined methods for determining acetone, alcohol and benzene in the air of factories. The results cited in the paper are sufficiently good for most purposes, and the methods may be found useful in similar cases.

Acetone.—After trying various reactions they used a process described by Messenger,[2] depending on the formation of iodoform when acetone vapour is passed through an alkaline solution of iodine (hypoiodite), and the consequent diminution of the iodine liberated on treatment with acid. The reaction is considered to take the following course, at any rate the initial and final states are as given:—

I. $2(CH_3)_2CO + 12KIO = 2(CH_3)COCI_3 + 6KOH + 6KI.$

II. $2CH_3COCI_3 + 2KOH = 2CHI_3 + 2KC_2H_3O_2.$

The net result is that two molecules of acetone correspond to six molecules of iodine (twelve atoms) or 1 c.c. of *N*/10 iodine to 0·000964 g. of acetone.

Elliott and Dalton[1] pass 10 litres of the air to be tested through an absorption apparatus containing 25 c.c. of *N*/10 iodine solution and 5 c.c. of 20 per cent. potash. After the air has slowly passed through it, the reagent is acidified with 2*N* hydrochloric acid, starch added, and the excess of iodine titrated back with *N*/10 thiosulphate solution.

Alcohol.—For determining alcohol the well-known reaction whereby alcohol is oxidised to acetic acid by chromic acid is utilised. The authors satisfied themselves that acetone did not interfere with this reaction by being itself oxidised, an important point, as the determination resolves itself into one of the residual chromic acid and not of the acetic acid produced. This latter, if it could be done, would have the advantage of being more specific.

For the determination the authors use in the absorption vessel 25 c.c. of a liquid made by mixing 100 c.c. of *N*/2 potassium bichromate, 100 c.c. of strong sulphuric acid and 50 c.c. of distilled water, which has been well cooled before taking the portion for the test. Air (10 litres) is slowly drawn through this, first passing through a tube with a plug of cotton wool to remove dust, since any matter oxidisable under these conditions will count as alcohol. The liquid is transferred to a flask, the residue in the vessel washed in with 45 c.c. of distilled water to make up the volume to 70 c.c. This is boiled under a reflux condenser for exactly fifteen minutes, cooled, 100 c.c. of 2 per cent. sodium iodide added (potassium iodide can be used) and the iodine liberated by the residual chromic acid titrated with *N*/10 thiosulphate and starch. A faint odour of acetic acid but none of acetaldehyde was observed after boiling, showing the completion of the reaction. One c.c. of thiosulphate corresponds to 0·00115 g. ethyl alcohol.

[1] *Analyst*, 1919, 44, 132. [2] *Ber.*, 21, 3366.

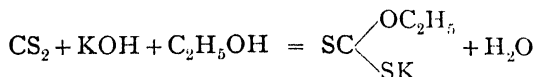
Benzene.—This determination depends upon the nitration of benzene to dinitrobenzene by a mixture of fuming nitric and sulphuric acids and the subsequent quantitative reduction of the nitro-compound by stannous chloride. Air (10 litres) is slowly passed through 15 c.c. of a mixture of equal parts of the two acids and then through 20 to 25 c.c. of 20 per cent. sodium hydroxide, to protect the connecting rubber tubing from attack by the acid fumes which are carried over from the first vessel. When all the air is passed, heat the absorbent for fifteen minutes on the water-bath to ensure complete nitration, cool, dilute, make just alkaline to litmus with about 50 c.c. of 40 per cent. sodium hydroxide, then faintly acid with hydrochloric acid, dilute to 500 c.c. to prevent crystallisation of the sodium salts, extract three times with ether and treat with about 0·5 c.c. of sodium hydroxide. After separation of ether from the soda and distillation of all that will come over, heat the residue on the water-bath to remove any oxidation products of alcohol and acetone, and dissolve in 10 c.c. of alcohol. The liquid is heated with 10 c.c. of a standard solution of stannous chloride for ten minutes, and then titrated with $N/10$ iodine. A blank experiment must obviously be made with a similar volume of stannous chloride at the same time as the determination, as this salt is very easily oxidised; in fact it would, in our opinion, be advisable to reduce the nitro-compound in an inert atmosphere, say, by passing carbon dioxide over the liquid.

Elliott and Dalton used Folin scrubbers which seem to be ordinary wash-bottles with the bubbler tubes blown out slightly and pierced with several holes; two were used for the acids and two for the alkali for the benzene process, and the four were bound to a block of wood for convenience in carrying about at the works where the determinations were made. Three aspirators were used so that all three vapours could be determined at once. Any other efficient scrubbers could be used; but care should be taken in making a choice, as the reactions used do not seem to be very rapid. The results appear to be accurate to about 10 or 12 per cent., which is good enough.

Carbon Disulphide.—The vapour of this liquid, which is used as a solvent for rubber and for other purposes in industry, is poisonous. Autenreith states that the following results were obtained from an investigation of this matter:—

Concentration of carbon disulphide per litre.		Effect.
to 0·15 c.c.	0·5 mg.	No injurious effect observed.
to 0·23 „	0·8 „	......
0·38 „	1·3 „	Slight uneasiness after several hours.
1·0 „	3·4 „	Uneasiness in thirty minutes.
1·76 „	6·0 „	Uneasiness in twenty minutes.
1·9 „	10·0 „	Paralysis, after-effects lasted several days.

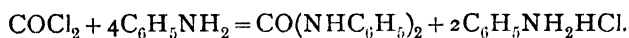
The method used by Autenreith is absorption by alcoholic potash whereby potassium ethyl xanthate is formed and titration of the xanthic acid, liberated by acidifying the solution, with standard iodine solution. The formation of xanthate proceeds thus:—

$$CS_2 + KOH + C_2H_5OH = SC\begin{cases} OC_2H_5 \\ SK \end{cases} + H_2O$$

The titration does not follow a very clearly defined course, but it is an agreed fact that one atom of iodine is required for one molecule of carbon disulphide.

From 10 to 20 litres of air is passed through a saturated solution of potassium hydroxide in alcohol in a Peligot absorption tube or other efficient apparatus. The vapour is absorbed quantitatively. The liquid is made up to 50 c.c. with 96 per cent. alcohol diluted with water, acidified with acetic acid and titrated with *N*/10 iodine solution. One c.c. of *N*/10 iodine corresponds to 7·6 mg. of carbon disulphide. This method appears to be chemically sound and quite specific.

Ethyl Ether.—The vapour of this substance can be determined, in the absence of carbon monoxide and acetone, by oxidation with iodine pentiodide. H. W. Haggard[1] finds that one molecule of ether liberates 4·8 atoms of iodine from the pentoxide when air containing it is passed over that substance heated to 200°. The arrangement is very similar to that used for the determination of carbon monoxide except that sulphuric acid must not be used for drying the air. Calcium chloride is used in its place and potassium hydroxide may be used to supplement the chloride. Acetone should be removable by bubbling the air first of all through a saturated solution of potassium or sodium bisulphite and then through, say, two tubes or other absorbing vessels, one containing a strong solution of caustic potash and the other crushed solid potash, to remove any sulphur dioxide which may be carried over.

Carbonyl Chloride (Phosgene).—It has been found by A. Kling and R. Schmutz[2] that a cold saturated solution of aniline in water will absorb completely as little as one part of carbonyl chloride in 100,000 parts of air. They bubble from 1 to 5 litres of air slowly, bubble by bubble through 10 c.c. of the solution in an efficient scrubber. The reaction is:—

$$COCl_2 + 4C_6H_5NH_2 = CO(NHC_6H_5)_2 + 2C_6H_5NH_2HCl.$$

The precipitate of diphenyl carbamide may be dissolved off the filter with alcohol, the solution evaporated, and the residue weighed, or it may after thorough washing be digested with sulphuric acid, and the ammonia thus produced determined by Nessler solution as in a micro-Kjeldahl.

[1] *J. Biol. Chem.*, 1923, **55**, 131. [2] *Comptes rend.*, 1919, **168**, 891.

II.—Suspended Matter in the Air

Besides gaseous impurities, air invariably contains solid particles of various kinds and sizes and may contain liquid droplets. That air is actually physically heterogeneous is shown by the fact that the path of a sunray in a shaded room or of the beam of a searchlight can be seen by the light reflected sideways by the particles. In a room the larger particles themselves can usually be seen. Their presence is also made evident as dust settling on furniture, etc.

This dust consists of the results of the wear and tear of practically everything solid upon the surface of the earth, of the salt of the sea projected into the air, with water as a spray, and left by the evaporating water as crystals, and, largely in towns, of finely divided sooty particles. Some of these particulate impurities are so finely divided that, once in the air, they fall only at an inappreciable rate and remain as a more or less permanent haze. Others may fall rapidly owing to large size or high density.

The amounts of some gaseous impurities in the air are so small that their determination is difficult, but the determination of suspended impurities presents even greater difficulty. The simple obvious method of passing air through a small tube with a closely packed cotton-wool or asbestos plug as filter is not really very practical, as even with a good micro-balance used with proper precautions the amount of air required to be passed through the filter is very large indeed. Certain methods are, however, available which give some, not very precise, indication of the amount of such particulate pollution.

In the relatively simple but important case of nuisance from grit—coal dust, coke and ashes—falling over a neighbourhood near a large chimney shaft, the source of these can be determined with some approach to certainty by collecting, in flat trays or large Petri dishes placed around the suspected source, the dust which falls in a defined time, noting the direction and strength of the wind during the period of collection. The amounts collected at the different stations are weighed and examined, first with a hand lens, then, if desired, under the lesser powers of a microscope, using illumination appropriate for opaque objects. The opinion as to the nature of the deposit formed thus can be confirmed by chemical means, *e.g.* by dry distillation in a small glass tube, demonstrating the presence of coal by the formation of tar and gas, or by determining the loss on ignition. The relative weights of the deposits considered with the relative positions of the stations and the prevailing winds should show the probable source of the deposit. If the heaviest deposits are collected to leeward of the suspected source, and with changes of wind the worst direction is always approximately that to which a vane on the suspected source would

point, the case may be considered as proved. If, on the other hand, there is no correlation between deposition and wind direction, or the heaviest collections are found on the windward side of the source, further investigation must be made.

When for any cause only one station is available, a series of observations over a period must be made and for each unit period—say each week—the mean direction of the wind estimated. This can be done graphically by drawing lines in the observed directions, of lengths proportional to the estimated velocity and connected in series, the second day's line commencing where the first day's left off, in the manner of the representation of forces in mechanics. By joining the ends of the compound line so formed one line is obtained representing the resultant of the wind directions and velocities for the week. The same thing could obviously be done by using the sine or cosine of the angle made by the wind with any chosen point of the compass and multiplying by the wind force, so that a series of positive and negative components on two rectangular axes could be obtained giving on addition and division a tangent or cotangent of the desired angular direction. The wind directions and weights of deposits can then be correlated and the direction from which the heaviest deposits come be determined.

Coarse pollution of this kind, by matters which settle easily, presents very little difficulty, but when the suspended matters are very finely divided the difficulties are very much greater. Only finely divided matters remain more or less indefinitely in the air, and cause general pollution spreading far from their place of origin.

There are some obvious methods of collection and estimation such as (1) settlement on small areas and counting, (2) filtration, (3) washing out by means of rain—a method not entirely satisfactory in dry weather—and others less obvious but still possible of application, including (4) projection in a current of air on adhesive surfaces, (5) condensation of droplets on the particles, (6) separation by electrical deposition (electrophoresis), as in the Cotterell method for cleansing air from particles, and others. Various pieces of apparatus have been designed based on one or other of these methods. We shall describe those of which we have personal experience and which have been found to give results which indicate at least orders of pollution, if not actual quantitative measures.

The most widely used method in this country for coarse matter is by means of the Deposit Gauge adopted by the Advisory Committee on Atmospheric Pollution, which started as a voluntary committee, then was connected with the Meteorological Office, and is now succeeded by a Research Committee of the Department of Scientific and Industrial Research, with the work of which we are both connected. It is used for systematic observations over the whole of the country

(that is, where co-operating bodies are to be found), and is adapted for this purpose rather than for investigations extending over a short period such as the chemist is likely to be asked to undertake.

The Deposit Gauge.—The standard deposit gauge consists of an open-topped funnel connected below with bottles. There are over eighty

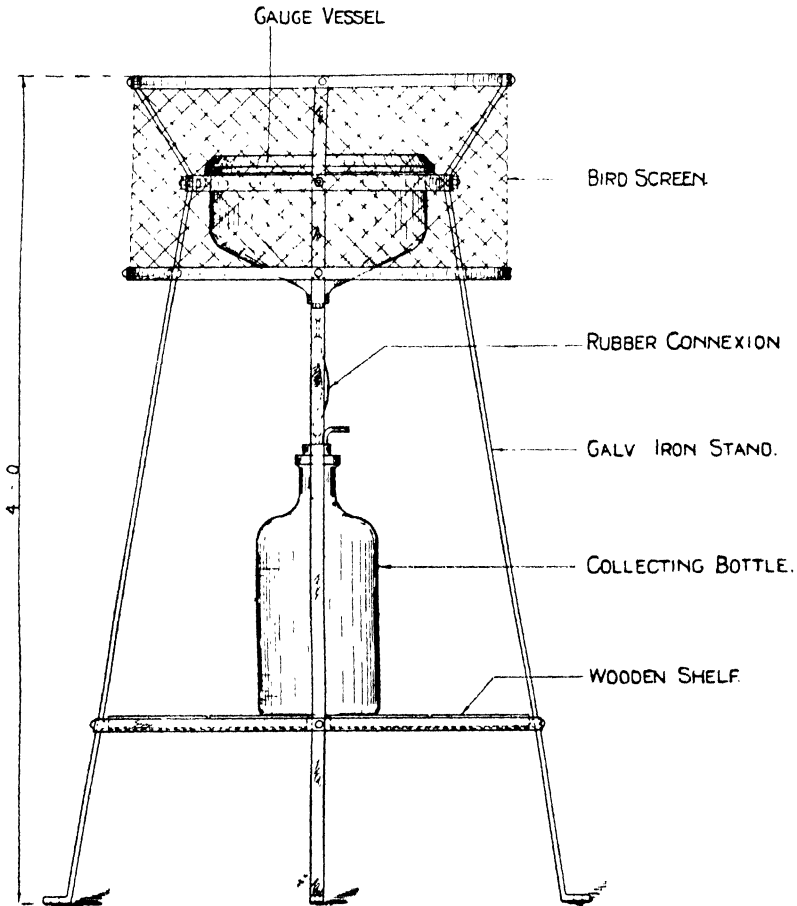



FIG. 97.

such gauges now in operation in different parts of the country. While there are two different types of gauge the fundamental principle is the same in each. The larger gauge consists of a circular enamelled cast-iron funnel about 70 cm. in diameter, whilst the other has a glazed stoneware or glass funnel of 30 cm. diameter (Fig. 97). Projecting above the gauge vessel is a wire screen, open at the top, intended to prevent birds from settling on the edge of the vessel. The vessel is conical at the bottom and communicates, by means of a glass tube and rubber

connection, with one or more bottles, designed to hold one month's rainfall. The rain and deposited matter falling on the gauge are collected in the bottles and removed once a month for analysis. The large size of the gauge is necessary to provide sufficient deposit for analysis. The inside of the gauges is washed down monthly with some of the collected water before the latter is removed for analysis. The deposited matter is divided into soluble and insoluble, and a partial analysis made of each, showing the tarry, carbonaceous or sooty and the insoluble mineral matter; the soluble part is divided into combustible or volatile matter and mineral matter. A further analysis of the soluble part is made into sulphates, chlorides and ammonia. It was felt that such a division gave the main constituents of the deposit which would be of interest, whilst a more complete analysis would have involved too much work, and therefore limited the scope of the inquiry. The authorities co-operating with the Committee make their own analyses and return to the Committee a monthly form, as shown herewith, in which the deposit is shown as grammes, per cent. of total solids and metric tons per square kilometre. The form has lately been modified to include also English tons per square mile. The nature of the deposit collected is shown in the table on following page, which is taken from *The Smoke Problem of Great Cities*,[1] and this serves to show the great variation in different places. Another point of great interest is the curious relation which the deposit of sulphates bears to that of total solids. In all cases it will be seen that as the total deposit goes up the percentage of sulphates falls.

From the figures for deposit collected over several years, it appears that the annual deposit in London has fallen from 415 tons per square mile in 1916 to 316 in 1928. In Glasgow, the deposit has fallen in the same period from 422 tons per square mile to 320. These figures show the marked improvement in the air of these two cities of recent years, and illustrate one of the uses of measurement.

The method of measuring deposit in this way has been criticised as giving results depending upon rainfall rather than upon quantity of impurity. The figures collected by the Committee indicate that the deposit of insoluble matter bears no relation to the rainfall, whilst a relation is observable between the deposit of soluble matter and the amount of rainfall. This is of interest as indicating the part played by the soluble impurities as nuclei of condensation.

In setting up these gauges great care has to be taken in the selection of suitable sites, and efforts are made to observe certain rules:—The gauge is set up in an open position, well removed from any special source of impurity. It must not be sheltered in any way, and should be a distance from any obstacles in its neighbourhood, such

[1] By Sir Napier Shaw and one of the Authors.

FORM 4761. No. of Report..................

Meteorological Office, Air Ministry, London.

ADVISORY COMMITTEE ON ATMOSPHERIC POLLUTION.

REPORT OF OBSERVATIONS FOR MONTH ENDING..192.........

Centre.. { Gauge No.............................. / Factor "F" for gauge...............

Collector..

Volume of Water Collected.....................................litres = ... Millimetres of rainfall

Total Solids dissolved...grammes } dried @ 100° C.
Total Insoluble matter..

Total Solids Collected...........................grammes = ... tons per sq. Kilometre

	Grammes.	% of Total Solids.	Metric tons per square Kilometre.
COMPOSITION OF UNDISSOLVED MATTER :—			
Soluble in CS_2 (tarry matter)..................	....	= .... %	....
Combustible matter insoluble in CS_2............	....	= .... %	....
Ash	....	= .... %	....
Total undissolved matter.........			
COMPOSITION OF DISSOLVED MATTER :—			
Loss on ignition..................................	....	= .... %	....
Ash	....	= .... %	....
Total dissolved matter.........			
Sulphate as SO_3................................	....	= .... %	....
Chlorine as Cl	....	= .... %	....
Ammonia as NH_3	....	= .... %	....

REMARKS :—

Signed.. Date..

as walls or buildings, equal to twice the height of the obstacle. The gauge is set up, when possible, upon the ground level, but the stand supporting the funnel raises the edge of the latter about 4 feet above the ground.

The Air Filter.—An instrument which has been found very useful for obtaining a continuous record of the smoke and dark dust in air of tunnels and places subjected to special local contamination is The Air Filter designed by one of us. This is made in two forms, one of which is portable and suitable for investigating the state of the air over a district or along the length of a tunnel. The other being a recording instrument which must be set up in a place with a constant supply of water.

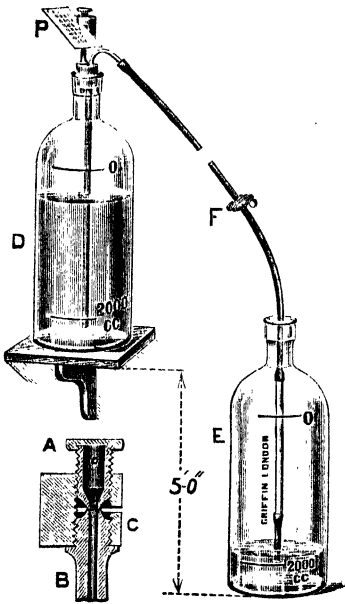
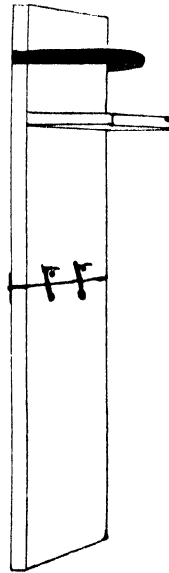



FIG. 98. FIG. 99.

The fundamental principle of the apparatus is as follows:—A measured and standard volume of air is drawn through a small disc of thick filter paper of standard diameter, leaving thereon a permanent record of the quantity of impurity present. This record is in the form of a discoloured disc, the shade of which indicates the amount of suspended impurity. The apparatus is intended to enable the purity of the air of cities to be compared, and records kept; hitherto no simple method for doing so has been available.

An observation can be made in about ten minutes, and a specially prepared and numbered scale of shades is supplied for comparing the degree of impurity of the air of different cities.

The apparatus consists of the filter proper, A, B, C, enlarged in Fig. 98, two bottles, D and E, a rubber bung with glass and rubber tubing, and a screw clip F, on the rubber tube. Record papers, P, are provided for taking observations. To use the apparatus, fill one bottle with water to the top zero mark, the other to the lower 2000 c.c. mark, fill the rubber tube with water by drawing out the air, and then close clip F. Fix the rubber bung tightly in the neck of the full bottle with the filter, glass and rubber tubing in position, taking care that lower end of the glass tube is just below the lower mark on the bottle. Place a slip of record paper in the slot in sleeve C, by slightly unscrewing plug A and then screwing down firmly on the paper. It is unnecessary to use great force in screwing down plug A, as a gentle pressure is sufficient to make a good joint round the filtering disc. Place the bottle with the filter on some support raised sufficiently to allow the lower end of the rubber tube to enter the neck of the other bottle

Form of Record Papers.

RECORD	●	⁘								
VOLUME	2L	2L								
SHADE No.	5	1								
TIME	10 am	10 am								
DATE	9 2 14	10 2. 14								
PLACE	London	London								
REMARKS	Foggy	Clear								

which is placed to receive it. This will provide a fall of about 5 feet for the water.

The apparatus is now ready to take an observation and this is done by opening the clip F, and allowing the water to flow from the upper to the lower bottle until the 2000 c.c. mark is reached; when this mark is reached the clip F must be closed. It takes about eight to ten minutes for the water to reach this level. After closing the clip F, the filter must be left untouched for two or three minutes to equalise the pressure inside and outside the bottle, after which the record may be removed by slackening plug A. In order to indicate when this equalisation has taken place, a short length of glass tube is fixed in the lower end of the rubber tube; by lifting this, opening clip, and placing the glass tube beside the upper bottle, the level of the water in the tube gradually rises to that in the bottle, when the record may be removed. If it is desired to repeat the operation, the lower bottle which has received the water may be substituted for the upper by changing the bung. The volume, shade No., time, date, place and remarks, such as "sunny," "thick fog," etc., should be entered on the

record slip on its removal. To find the shade on the scale corresponding with the record obtained on the filter paper, pass the latter gently under the scale between it and the card on which it is mounted, and so that the record is seen through the hole in any shade. Holding in a direct good light the shade corresponding to the record can thus be easily found. Enter the shade number in the space provided for it on the record paper. Do not touch with the fingers (*a*) the part of the filter paper on which the records are taken, or (*b*) the shaded part of the scale.

We have found a support similar to Fig. 99 very convenient for supporting the bottles during use. It will be seen that the main board hinges in the middle so that it can be carried in a car with any other gear which may be used.

If the records are taken on pure (acid extracted) filter paper, the darkened discs can be used for microchemical analysis after the tint has been evaluated if this be desired.

The Automatic Recording Air Filter.—This instrument, Fig. 100, is designed to measure the density of city fogs by an automatic arrangement which causes 2 litres of air to be filtered, at regular intervals, through an $\frac{1}{8}$ inch diameter disc of white filter paper. The records obtained consist of dark spots $\frac{1}{8}$ inch diameter round the edge of a large paper disc, 7 inches diameter, the latter being divided into 24 hours, similarly to a clock face. The density is read by comparing the records with a calibrated scale of shades from white to nearly black in ten steps, the shades being numbered 1, 2, 3, 4, 6, 8, 10, 12, 15, 20, which numbers represent quantities of impurity, the value of 1 on this scale being ascertained by calibration to be 0·32 mg. per cubic metre.

The instrument consists of the main vessel (1) into which water is admitted through an inlet (7) at the bottom. A siphon fixed inside the vessel causes the water to rise and fall between two fixed levels, thus alternately driving air out of the vessel and drawing it in through the air inlet plug (23). This plug is hollow and slides up and down in an air inlet sleeve which has a horizontal slot in which the edge of the filter paper disc is placed. When air is drawn in, the air inlet plug is automatically brought down on the filter paper disc so as to make an air-tight joint, and all air drawn into the main vessel must pass through the filter paper; the impurities are left behind on it and a small black disc or spot is made. When the siphon has finished working and the water rises again, the pressure on the air inlet plug is automatically released, the counterbalance weight lifts it and the disc is free to move.

The air inlet plug is made to bear on the filter paper in the following way:—Inside the main vessel (1) is a bell with its mouth downwards;

this is mounted on a central rod which has at its bottom the valve sleeve; when the water is at the higher level the bell is full of water, and when the siphon acts, and the water level falls, it cannot fall inside the bell, because the air cannot enter. The weight of water inside the bell pulls it down and the central rod with it, closing the water valve, pulling down the control arm and thus forcing the air inlet plug (23) down on the filter paper. Then, since air can only

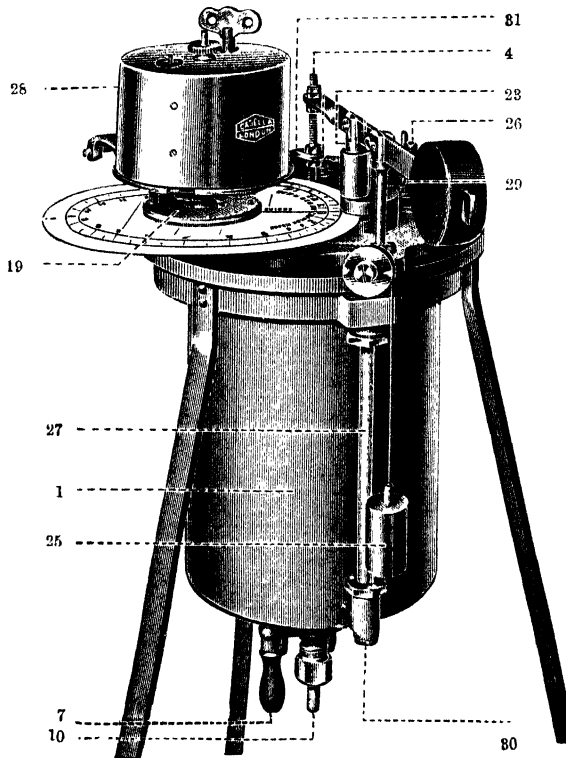



Fig. 100.

1. Vessel. 4. Adjustable Connecting Rod. 7. Water Inlet. 10. Water Outlet. 19. Turntable. 23. Air Inlet Plug. 25. Weight. 26. Manometer Cock. 27. Gauge Glass. 28. Clock. 29. Air Inlet. 30. Plug for fixing Gauge Glass.

enter through the filter paper, the pressure in the main vessel falls as the siphon draws the water out; there is then a pressure of air on the top of the flexible diaphragm which is attached to and also presses down the central rod. When the level has fallen sufficiently, air can enter the bell and the water falls out, but the diaphragm keeps the plug (23) pressed on to the filter paper.

The water level continues to fall till the siphon breaks and the air in the main vessel returns to atmospheric pressure; when the counter-balance weight lifts the central rod and the air inlet plug, it also opens

the water valve by lifting the water valve sleeve, which admits water and the level again rises. The air in the main vessel is now free to pass out through the air inlet sleeve. The bell has a small float valve which lets out the air as the water rises, and allows the bell to fill with water; the float valve, however, will not allow air to enter the bell when the water falls.

After each record has been taken, the filter paper disc moves through a small angle and the next record is made at a different place. In order that the disc may move in this way, it is mounted on a turntable (19) revolving on a central pivot and operated by a cord passing over a pulley with a weight (25) attached. The turntable is controlled by a clock, which has a boss with an arm on it engaging one of the studs on the turntable; this arm makes one revolution in 24 hours. The weight keeps the stud on the turntable pressing against the arm on the clock boss, except when a record is being taken, during which the disc is held by the air inlet plug and the turntable cannot turn; the arm on the clock boss moves on until the air inlet plug is lifted, and the turntable is again free to move, and its stud can follow up the arm. Thus each record is placed automatically on the filter paper disc opposite the time when it was taken. In this way 2 litres of air is drawn through the filter paper disc at regular intervals, leaving records of the impurities present in the air.

To put the filter in working order, the nuts on the central rod (4) should be slackened from the stop bracket (31), and care should be taken that the nuts at the top end of the central rod (4) do not grip the arm (16) but allow it to move freely while transmitting movement to the central rod. Adjust the balance weight (17) so that the central rod (4) is just lifted by the control arm; when the central rod is in its highest position the water valve sleeve should just uncover the hole in the water valve; this can be tested by blowing through the tube connected to the water inlet cock (7). The water inlet cock is connected to a suitable water supply by means of rubber tubing, and a rubber tube is fixed to the water outlet (10) to allow the water to run to waste. By reducing or increasing the water supply the time between the records may be made greater or less, but care should be taken not to have a greater flow of water than the siphon can carry off, or the filter will not work. If it is seen that the water in the gauge glass (27) falls slowly when the siphon begins to work, then the flow at the water inlet is not too great. The rubber tube fixed to the water outlet should be at least 4 feet long, its end should hang free and should not be allowed to dip into the water. When the siphon is first started, or when it has not been used for some time, the inside will be quite dry; this will greatly influence the working of the siphon owing to capillarity; therefore it should be started the first time by

sucking the end of the rubber connection on the water outlet (10). When once the siphon has become wet, it will continue to work regularly.

The filter disc is fitted by lifting the clock, and removing the top plate of the turntable; the three holes in the disc fit over the central pivot of the turntable and over the two studs on the turntable. The edge of the disc must be placed in the slot in the air inlet sleeve. The top plate is replaced and keeps the disc in position, a piece of cord 12 inches long is threaded through the hole under the turntable and is passed over the pulley and attached to the weight (25). Wind the clock and set it going, see that the disc is quite free to turn. Turn the disc round in a clock-wise direction so as to wind up the cord, and lower the clock on to the turntable (19) so that the arm on the clock boss engages with one of the studs and the filter is left for twenty-

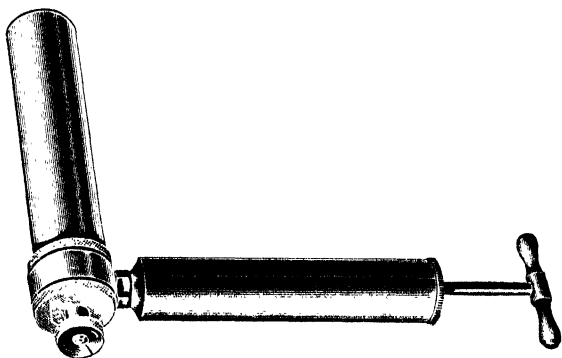



Fig. 101.

four hours, when a new disc must be fitted on the turntable. The disc is set with the correct hour opposite the air inlet plug (23) by turning the knob on the top of the clock. The water is then turned on. When fitting or removing a disc, care must be taken not to touch the edge or it will be soiled by the fingers and the records will be smudged. The clock must be wound once a week.

Immediately the disc with the records has been removed, the date, place and nature of the weather should be entered on the face in pencil.

The Air Filter was very carefully calibrated by one of us and Mr J. G Clark and the shades on the scale supplied with the instrument correspond to known amounts of soot. Recently the shades have been carefully evaluated in terms of proportions of black and white so that they do not depend upon the care with which the original paper scale has been kept.

The Dust Counter.—The third method of investigation used is the jet dust counter devised by one of the authors. It will be evident that the automatic filter depends for its indication upon the colour of the

impurity and gives little information as to its nature; hence something else was required, and the jet dust counter[1] was evolved. An impact method is used; great precautions are taken to get the highest possible efficiency. For example, the jet of air which is caused to impinge is made excessively thin and flat like a ribbon. In the standard instrument it is 1 centimetre wide and 0·1 millimetre thick. It is caused to strike a microscope cover glass at such a high velocity that the adiabatic expansion and cooling of the air brings about con-

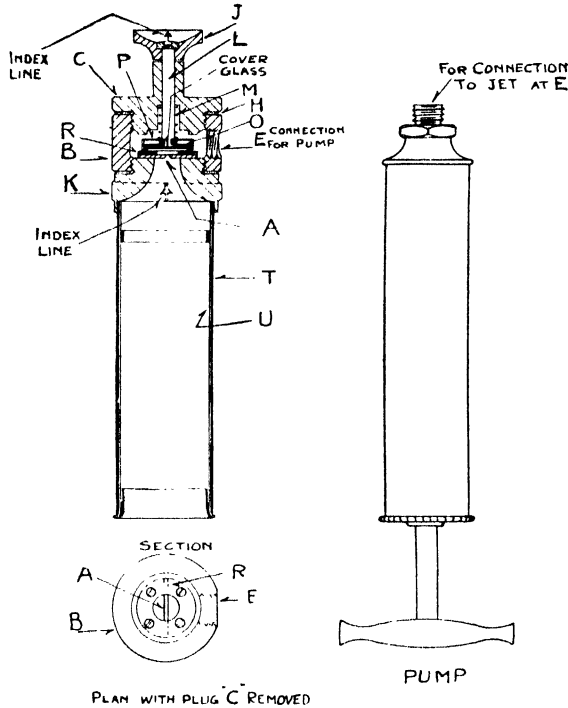



FIG. 102.

densation of water upon the dust, or at least upon many of the dust particles, and the line of impact of the jet upon the cover glass is wetted in this way, causing the dust to adhere. When the jet impinges it is deflected laterally in two very thin films of air which are so shallow, owing to the thinness of the jet, that the high velocity enables the dust particles to penetrate to the bed of the air stream and to strike the cover glass. The instrument is illustrated in Figs. 101 and 102.

It consists of a head containing the slot for forming the jet, an air pump to draw the air through the jet, and a damping chamber through

[1] *Proc. Roy. Soc.*, 101, A., 1922.

which the air must enter, and where it may pick up sufficient water to act as an adhesive. When taking a record, the screw plug C is removed, and the damping chamber filled with the air to be tested by making a few strokes of the pump; a thoroughly clean cover glass is placed in the cell R, the plug C screwed home and the handle of the pump withdrawn as rapidly as possible. It is useless to draw the air through slowly, as the velocity will not be sufficient to give high efficiency. The pump piston is therefore withdrawn as instantaneously as possible so that the air will enter at its maximum velocity, which is about that of sound, and impinge upon the cover glass, where it deposits its dust. The apparatus has been tested for efficiency in several ways:—An instrument was prepared having two cells, one above the other, and two slots in series, but staggered, so that the air drawn through the first slot impinged upon the roof of its cell and passed on to the next slot, impinging upon the roof of the second cell. The floors and roofs of these cells were made of glass, so that the process could be watched under the microscope, and an indication of the efficiency was given by the number of particles trapped upon the roof of the second cell. Obviously, if all were caught in the first cell none would appear in the second. Tested in this way, with the damping chamber in position, practically all the particles were found to be trapped in the first cell. Without the damping chamber, in dry weather, the efficiency is not nearly so high. Again, air which had passed through the jet was subsequently drawn through a paper filter known to trap all the dust, but did not then produce a discoloration.

The record obtained in this instrument is a linear trace of dust 1 centimetre long across the cover glass. It is mounted, record downwards, over a metal or paper ring upon a microscope slide, and is then ready for examination. The linear form of the record permits it to be easily found by using a low power, such as a $\frac{2}{3}$ in. objective, and dark ground illumination. The record having been found, the high power is moved into position, and the dust particles can then be examined under a $\frac{1}{12}$ in. oil immersion objective. It will be understood that, although the particles are not embedded in a medium, they are in contact with the under surface of the cover glass, and that therefore there is no air gap to spoil the resolution of the oil immersion objective. The particles can be counted by means of a net-ruled micrometer, examined and measured if desired. In this way it is found that the air of London on an ordinary winter's day contains from 5000 to 10,000 particles per cubic centimetre, but that during a dense smoke haze the number rises to 60,000 or 80,000. The dust particles are mostly small, averaging about 0·7 to 0·8 microns, and rarely exceeding 2 microns, and always scattered amongst the irregular black particles are a certain number of spherical transparent balls of

a diameter up to $1\frac{1}{2}$ microns or 2 microns, sometimes colourless and sometimes yellow or ruby. These are doubtless particles of fused ash from fires. During dense smoke haze the average size of the particles is greater.

A second method of using the instrument may be of interest:—It will be understood that the adhesion of the particles depends upon the condensation of water, and this water, if there is not enough in the air, is supplied from the damping chamber. A volume of 50 c.c. is found to provide a record nicely scattered and suitable for counting in London air. If a larger volume, say 1000 c.c., be drawn through, the particles are piled one on top of the other, and if, at the same time, the damping chamber be held in the hand so as to warm it slightly, enough water is condensed on the record to be blown out sideways in definite streams. In the head of these streams, which dry up immediately, are found crystals of the soluble salts present in the dust. The examination of these crystals provides a means of identifying the salt present.

Another method of examination is to take a very dense record on the cover glass and support a second cover glass about 1 millimetre above it, the record being enclosed between the two. A drop of water placed on the top cover glass keeps it cool, while the lower one, with its record, is heated. Treated in this way, it is found that a line of oil drops is often deposited on the upper glass over the line of dust on the lower one. Such drops from London records are soluble in xylol but not in water, and, no doubt, are derived from tar in the soot.

Still another method of utilising the instrument is to take records upon prepared cover glasses on which a dilute solution of methyl orange has been allowed to evaporate, covering the glass with small crystals. The dust impinging upon the prepared surface, and being wetted at the same time, acts upon the methyl orange, forming crystals characteristic of the acid or alkaline salt. For example, during a dense London fog on 22nd January 1922, the dust examined in this way was definitely acid, whereas a few days previously a definitely alkaline reaction was obtained. A modification of this method has been tried in which two half-discs of filter paper have been fixed upon a thin ring so as to fit in the instrument instead of a cover glass. One half-disc was coloured with methyl orange or congo red made slightly acid, and the other with the same indicator slightly alkaline, but both as nearly neutral as possible consistent with distinct coloration. The record was then taken across the junction of the half-discs, and the colour change on the paper observed.

In the examination of the soluble salts found in these records there is considerable difficulty, since the crystals obtained are very small. One of the authors has sometimes obtained records consisting of practically

nothing but crystalline matter; one group of such records was obtained during a warm, sunny day with a bluish haze on the sea-coast in the south of Portugal. All the particles of the haze were obviously common salt, or at least sea salt. Another remarkable record of a similar type was obtained in the Gulf of St Lawrence. Here there was a white haze and brilliant sunshine, and the record also consisted entirely of soluble crystalline matter. These crystals are too small to give characteristic effects under polarised light, as they can hardly be regarded as transparent. Methods of microchemical examination have been attempted but not with very great success. For example, a reagent was sprayed into the air, and when the spray had practically all disappeared a cover glass was held under it and a few minute drops were found to have settled on this. This cover glass was then mounted in a special instrument, drops downwards, and over, but separated from, a second cover glass, with the crystals to be examined. On breathing towards the crystals, being hygroscopic, they collected water and dissolved. Keeping them under observation under the microscope the drops of reagent and solution were brought into contact. The test was on such an excessively small scale that, although characteristic reactions were sometimes obtained, this was not always so.

The following are typical counts of records which afford comparison of the state of the air in different localities:—

Date, 1922.	Place.	Time (Summer Time).	No. of Smoke Particles per c.c.	Remarks.
Saturday, Sept. 2	Holme, Norfolk	12 noon	152	Country air, no chimneys near
Tuesday, „ 5	Brighton	12.10 P.M.	1,380	Wind NE'N.
Thursday, „ 7	Hull, near Victoria Pier	7.30 A.M.	4,830	Thick water fog
Friday, „ 8	„ „ „	7.15 A.M.	8,100	Wind NE'N. Smoke haze
Sunday, „ 10	„ „ „	6.30 P.M	3,080	Wind NE'N. Air obviously clearer
Monday, „ 11	„ „ „	7.30 A.M.	13,800	Wind W. Thick smoke haze
„ „ 11	Outside Spurn Point	4.30 P.M.	140	Haze visible over land

The Settlement Dust Counter.—Yet another piece of apparatus is available for counting the number of dust particles in a defined small volume of air. This is applicable in cases where a large proportion of the dust is likely to be other than soot, *e.g.* in the neighbourhood of a flour mill. In such a case a counting method is likely to be of more use than a colorimetric one although useful filter

records could probably be obtained on black paper such as is supplied by some makers of filter paper.

The object of this instrument is to enable a true count of the number of dust particles or bacteria contained in the air to be obtained, even when such dust particles are very coarse. It was designed primarily for an investigation into the dust pollution of the air of grain unloading stations. The ordinary method of exposure of a plate or dish for a given time, while giving a roughly comparative result, has little value as a quantitative method, since the amount of dust deposited upon a plate exposed in the open depends upon many variable factors, such as the size of the dust particles, their density, the temperature and degree of turbulence of the air; while, in addition, the deposit is obtained from an unknown volume of air. The present instrument

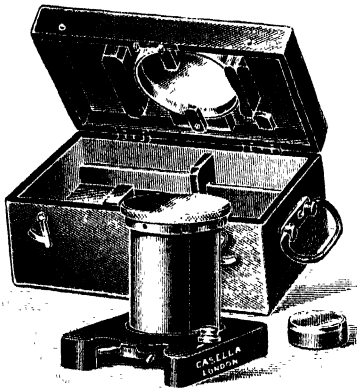



Fig. 103.

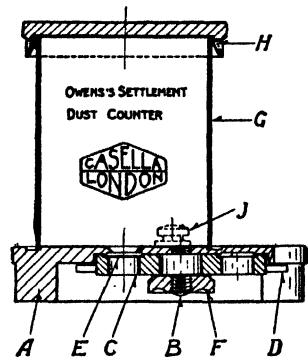



Fig. 104.

is designed to eliminate these uncertainties. Its working depends on the principle of enclosing a definite volume of air to be tested in a small vessel, with suitable precautions, the height of the vessel being known. The dust in a column of air of this height is allowed to settle upon the surface of a cover glass, where it is subsequently counted. Thus, the area of the base and the height of the column being known, the amount of dust per unit volume of air can be calculated. To permit the measurement of bacteria, this dust counter is of such design that it admits of being easily sterilised by heating.

The instrument (Figs. 103 and 104) consists of a heavy platform, or bedplate A, on the upper surface of which a cylindrical air vessel G, open at both ends, is placed. An annular ring is formed in the upper surface of this bedplate to receive the lower end of the cylindrical air vessel. A loose cap H is also provided for closing the upper end of the air vessel. It will be observed that the air chamber G is a plain open-ended metal tube. It is made in this form intentionally to permit

it to be easily filled with the air to be tested, by sweeping it axially through such air, and also in order that vessels of different height may be used if desired. The diameter of the air chamber is made very large compared with that of the cover glass, with the object of eliminating any effect which might be produced by the sides of the vessel.

Situated centrally under the axis of the air vessel is a circular hole penetrating the bedplate, which permits dust settling from the air to pass through it on to a microscope cover glass placed beneath the hole, as subsequently described. The under surface of the bedplate has a circular recess formed therein, eccentric to the axial hole, which recess receives a disc-shaped drum, pivoted at its centre to the bedplate by a pivot B, and held in position by a knurled nut F. Around the circumference of the drum capstan arms D project, by which it can be revolved round its pivot. The stop J serves to limit the rotation of the drum. The drum has six equidistant holes and the upper part is recessed to receive cover glasses. These holes lie on a circle concentric with the drum, and the number of capstan arms projecting from the drum is equal to the number of holes and cover glass recesses. Thus, the standard instrument has six holes with six recesses for cover glasses, and consequently there are also six capstan arms. The stop J is so disposed that when one of the arms engages it, a hole with its recess appears centrally under the axial hole in the bedplate under the middle of the air vessel. An annular groove is formed on the underside of the bedplate above the holes and recesses, so that the cover glasses are held in position. An index with numbers on the side of the bedplate indicates the number of the cover glass appearing under the air vessel.

The object of the design is to enable a representative sample of air to be enclosed in the air vessel and subsequently to permit of the simultaneous closing of the top of the air vessel and exposure of the cover glass. The need for this arises from the fact that immediately the cap is placed upon the top of the vessel the air is imprisoned and, since settlement is going on all the time, any interval between the closing of the top of the vessel and the exposure of the cover glass would introduce error. Surrounding the rim of the cap is a series of open holes, to prevent the imprisonment of excess air when placing the cap in position upon the air vessel. If any excess air were thus imprisoned, it would escape partly through the hole exposing the cover glass and might cause a deposition of dust during its passage. There is very little probability of this occurring with the arrangement shown.

The instrument may be used in two ways:—The first method is intended to provide a means for grading the dust, that is, ascertaining

the time required for settlement of the different sized particles, and also the numbers of each grade. This is necessary in order to ascertain the time of exposure to settlement which is required to obtain a true record of the amount of dust of any particular size or shape. To use the instrument in this way, five of the recesses in the drum are provided with clean cover glasses, the sixth is left empty, and when the drum is replaced the empty hole is put under the air chamber. The air vessel is removed and the instrument placed in the air to be tested. The air vessel is next swept axially through the air and placed upon the bed-plate in its annular recess. The stop J is next adjusted by making a complete revolution of the knurled head in an anti-clockwise direction. This moves the stop to the other side of the capstan arm engaging it, which is pushed slightly forward in the process. The drum is then free to revolve when required, so as to expose a cover glass; the cap H, which has been placed mouth downwards to prevent contamination with dust, is now placed upon the top of the air vessel, while simultaneously the drum is revolved to bring cover glass No. 1 in position under the air vessel. The stop J is again moved so that cover glass No. 2 may be brought into position when necessary, and after a measured interval has elapsed, cover glass No. 2 is revolved rapidly into position; the same process is repeated for the glasses Nos. 3 to 5, the interval for settlement depending upon the nature of the dust. On removal of the drum the five cover glasses will have deposited upon them fractions of the total dust which settled in the intervals given. Thus, by examination of these records, the time required for settlement of the dust it is desired to examine may be ascertained.

Having ascertained the time of exposure, the required records may then be taken as follows:—Three cover glasses are placed in the revolving drum in their recesses, leaving three alternate holes without any cover glasses, the cover glass being thoroughly cleaned before being placed in position. The drum is replaced in the bedplate, the knurled nut F screwed home and the stop J so adjusted that a hole in the drum comes under the hole in the bedplate in the axis of the air vessel. The instrument is then taken into the air to be sampled, and having placed the bedplate on a suitable bench or support, the air vessel is removed, the bedplate is waved through the air to fill the cell at the bottom of the air chamber with the air to be tested, after which the air vessel is passed two or three times axially through the air and brought down on to the annular recess on the top of the bedplate. The stop J is next revolved through a complete revolution in an anti-clockwise direction, causing the revolving drum to move slightly and shifting the stop-pin to the opposite side of the capstan arm with which it was in engagement, thus leaving the drum free to revolve when required. The cap for closing the top of the cylinder is next taken in

one hand and placed upon the top of the air vessel, while simultaneously the revolving drum is moved by the finger of the other hand until brought up by the contact of one of the capstan arms against the stop. This brings a cover glass under the hole in the top of the bedplate and, after a suitable interval is allowed to elapse for settlement, depending upon the nature of the dust being sampled, the drum is again revolved so as to bring the exposed cover glass under the shelter of the bedplate. The test may be repeated, using a second or third cover glass if so desired, after which the instrument is removed to clean air, the revolving drum taken out and the cover glasses mounted. If the dust record obtained is too light it may be repeated as often as desired, using the same cover glass, or a higher air chamber may be substituted.

When the air vessel, having been filled with the air to be tested, is placed upon the bedplate, settlement of the dust commences, but as the top of the air chamber is open no error is introduced in the dust count, since dust which settles out at the bottom, falling through the open hole in the revolving drum, is replaced by a corresponding amount of dust, which settles into the open upper end of the air vessel. It is only when the vessel is closed by the cap H that settlement inside becomes important, and to avoid error then, as already pointed out, the closing of the vessel and the exposure of the cover glass must be simultaneous.

In order to make the records permanent, it is necessary to treat the cover glass before exposure, so that the deposited dust will adhere thereto. To do this a very weak solution of Canada balsam in xylol is prepared, containing approximately 10 per cent. of Canada balsam. The cover glass, having been thoroughly cleaned, is taken in a forceps and one-half is dipped in the solution, the remaining half being kept dry. The cover glass is lifted slowly from the liquid so as to allow all excess to flow away from the glass, and allowed to dry, which it does in a few seconds, leaving an excessively thin continuous film of hard balsam on the part of the surface which was immersed. A sufficient number of cover glasses are prepared in this way and kept in the dust-proof receptacle provided with the instrument. After taking a record, the drum containing the cover glass is removed and placed under a glass cover provided, the roof of which has a disc of white blotting paper which is previously moistened by the addition of a few drops of xylol. In a few seconds the film of Canada balsam on the cover glass is softened by the xylol vapour and the dust particles adhere firmly. On removal of the cover, the balsam rehardens in a few seconds, when the records may be removed and mounted upon slides prepared with rings coated with adhesive, in the manner described for mounting the records of the jet dust counter.

Cover slips on which dust is deposited without any adhesive, discharge their dust very easily; the cleaning of the glasses may

electrify the surface, and on touching the cover glass to mount it, the dust is sometimes driven off and all deposited on the bottom of the cell. The dust cannot be mounted in Canada balsam in the ordinary way, since the particles become detached from the glass and lose their relative positions, so that it becomes impossible to count the record. Moreover, many of the particles, being practically transparent, almost disappear when immersed in Canada balsam. The portion of the cover slip left uncoated with balsam permits the particles to be examined dry, if so desired. The cover glasses, having been mounted in position on their cells, the film of balsam on the upper surface may be removed before examination by wiping with a cloth damped with xylol.

For examination of the particles and counting, a low power, such as a $\frac{2}{3}$ in. objective, may be used, and it is advantageous to use dark ground illumination. A square ruled micrometer eye-piece, having 1 mm. squares, such as is used in connection with the jet records, is calibrated by means of a stage micrometer, so that the area covered by the squares is known. The number of particles on the record is then counted inside a definite number of squares, from which figure and the height of the air chamber the number per unit volume can be ascertained.

The instrument is intended for use in dusty air where coarse dust particles are settling rapidly, and therefore it will soon become coated with dust and should be carefully cleaned after use and before replacing in its box.

The cover glasses which have been previously prepared with balsam must be protected from dust while placing in the instrument; should dust settle upon them, it may be removed by using a clean camel's-hair brush, or by blowing upon the surface, but it is preferable never to attempt to place clean cover glasses in position in very dusty air.

The Settlement Dust Counter above described is not suitable for excessively fine dust, such as forms the smoke haze in a city. A modification of the instrument by which the settling chamber is made air-tight, so as to prevent "breathing" due to changes of pressure or temperature, makes it suitable for fine as well as coarse dust. The long period required for very fine dust to settle makes it necessary to take great precaution against changes of temperature during settlement, as such changes cause convection currents within the chamber and falsify the result. Similarly, care must be taken that the cover glasses used to receive the deposit are not charged electrically by rubbing during cleaning, or if so charged are discharged before placing in the instrument.

Another method which has been tried for counting suspended dust is the use of the ultramicroscope. This is simply a modified form of

dark ground illumination used with an ordinary low power microscope. A very intense light is directed on the dust particles while enclosed in a small special cell and at such an angle that the direct rays cannot enter the objective of the microscope. Thus the dust particles are shown up as brilliantly illuminated points on a dark background.

Owing to the Brownian movement of the dust and the continual settlement of the particles, it is not possible to use a high magnification with this method: the highest power objective suitable is about $\frac{2}{3}$ in. The method has certain fundamental objections, notably that the number of dust particles brought into view depends very much on the intensity of illumination used.

Other methods may suggest themselves to the analyst as suitable for his special purposes. The whole subject of suspended matter is still in the experimental stage, and the methods given above are those we have so far found to be the best available for the purposes for which we have needed them.

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Atomic Weights (1925)

	Symbol.	Atomic Weight.		Symbol.	Atomic Weight.
Aluminium	Al	26·97	Molybdenum	Mo	96·0
Antimony	Sb	121·77	Neodymium	Nd	144·27
Argon	Ar	39·91	Neon	Ne	20·2
Arsenic	As	74·96	Nickel	Ni	58·69
Barium	Ba	137·37	Niobium Nb (= Columbium Cb)		93·1
Beryllium Be (= Glucinum Gl)		9·02	Nitrogen	N	14·008
Bismuth	Bi	209·00	Osmium	Os	190·8
Boron	B	10·82	Oxygen	O	16·000
Bromine	Br	79·916	Palladium	Pd	106·7
Cadmium	Cd	112·41	Phosphorus	P	31·027
Caesium	Cs	132·81	Platinum	Pt	195·23
Calcium	Ca	40·07	Potassium	K	39·096
Carbon	C	12·000	Praseodymium	Pr	140·92
Cerium	Ce	140·25	Radium	Ra	225·95
Chlorine	Cl	35·457	Radon	Rn	222·
Chromium	Cr	52·01	Rhodium	Rh	102·91
Cobalt	Co	58·94	Rubidium	Rb	85·44
Copper	Cu	63·57	Ruthenium	Ru	101·7
Dysprosium	Dy	162·52	Samarium	Sa	150·43
Erbium	Er	167·7	Scandium	Sc	45·10
Europium	Eu	152·0	Selenium	Se	79·2
Fluorine	F	19·00	Silicon	Si	28·06
Gadolinium	Gd	157·26	Silver	Ag	107·880
Gallium	Ga	69·72	Sodium	Na	22·997
Germanium	Ge	72·60	Strontium	Sr	87·63
Gold	Au	197·2	Sulphur	S	32·064
Hafnium	Hf	178·6	Tantalum	Ta	181·5
Helium	He	4·00	Tellurium	Te	127·5
Holmium	Ho	163·4	Terbium	Tb	159·2
Hydrogen	H	1·008	Thallium	Tl	204·39
Indium	In	114·8	Thorium	Th	232·15
Iodine	I	126·932	Thulium	Tm	169·4
Iridium	Ir	193·1	Tin	Sn	118·70
Iron	Fe	55·84	Titanium	Ti	48·1
Krypton	Kr	82·9	Tungsten	W	184·0
Lanthanum	La	138·90	Uranium	U	238·17
Lead	Pb	207·20	Vanadium	V	50·96
Lithium	Li	6·940	Xenon	Xe	130·2
Lutecium	Lu	175·0	Ytterbium	Yb	173·6
Magnesium	Mg	24·32	Yttrium	Yt	88·9
Manganese	Mn	54·93	Zinc	Zn	65·38
Mercury	Hg	200·61	Zirconium	Zr	91·

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